United States
Department of
Agriculture

**Agricultural
Research
Service**

1995–1

November 1994

Starch-Encapsulated Pesticides

ARS Papers Presented at the International Seminar on Research and Development of Controlled-Release Formulations of Pesticides

Vienna, Austria
September 6–10,1993

Doan, William M., and Marvin M. Schreiber, eds. 1994. Starch-Encapsulated Pesticides: ARS Papers Presented at the International Seminar on Research and Development of Controlled-Release Formulations of Pesticides, Vienna, Austria, September 6–10, 1993. United States Department of Agriculture, Agricultural Research Service, 1995–1, 87 pp.

While supplies last, single copies of this publication may be obtained at no cost from the William M. Doane, National Center for Agricultural Utilization Research, 1815 North University Street, Peoria, IL 61604.

Copies of this publication may be purchased from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161; telephone (703) 487–4650.

Issued November 1994

Contents

STARCH-ENCAPSULATED PESTICIDES—STATUS REPORT

Executive Summary

Advanced technology for encapsulation of pesticides within a starch matrix by extrusion involves entrapment without cross-linking chemicals, ancillary polymers or modification of starch substrate. Solid, crystalline, and liquid pesticides have been successfully entrapped in unmodified starch matrices by a continuous, twin-screw extrusion process.

Starch Encapsulation by Extrusion Process Versatile and Cost Effective

Matrix composition and processing conditions can be selected to maximize encapsulation efficiency, and optimize performance of the starch encapsulation product. Type of starch, addition of filler, physical form, level of active agent, and amount of water are variables considered in designing the matrix. Temperature profile, screw design, degree of mixing, extent of shear, screw speed, and residence time are processing variables readily controllable to modify properties of the granular product. Total solids level (starch plus active agent) of up to 75% easily processed in the twin-screw extruder to yield a product requiring a minimum amount of drying.

The twin-screw continuous process is flexible in process design due to its "building block" feature. The process section is composed of segmented units which can be pieced together to suit a unique set of process and mixing requirements. The advantages of the modular design include high degree of freedom in barrel arrangement and flexibility in altering the shear, mixing, and residence time distribution. Process optimization results when screw intensity is sufficient to create an amorphous melt and distribute active ingredient (a.i.) within the melt, but gentle enough to minimize heat generation from numerous sources of shear stress to attain maximum flow rate.

A cost analysis estimate scaled up to annually produce 40 million pounds of product would be \$0.033 per pound for conversion using the twin-screw extrusion technology. Total production cost would depend on the cost of the a.i. and could be as low as \$0.335 per pound of product for a raw material cost of \$0.299 per pound. These are significantly below the target costs proposed by industry.

Starch-Encapsulated Formulations Effective and Environmentally Friendly

Several environmental factors directly affect the release rate (RR) of starch encapsulated (SE) formulated herbicides. As starch granules imbibe water they swell and allow the herbicide entrapped to diffuse out of the granule. At saturation, complete loss of atrazine and alachlor was obtained in 21 days and 7 days, respectively. At +1.5 MPa, <50% of atrazine and <80% of alachlor was released from the starch granule after 28 days. Increased temperature and microbial activity increase the RR from SE formulations.

Leaching trials using packed soil columns and intact soil blocks showed reduced atrazine leaching by 65 to 85% of the leaching of commercial formulation (CF). Field trials have confirmed these laboratory tests. Surface runoff of atrazine as a SE formulation was reduced 80% compared to the CF in field trials under high rainfall. Similarly, atrazine concentration in tile drains runoff was significantly reduced when in a SE formulation thus preventing large flushes of atrazine in surface and groundwater when heavy spring rains follow initial atrazine application.

Regardless of how environmentally safe or cost effective a new herbicide formulation may be, to be adapted, its herbicide efficacy measured by weeds controlled and affects on crop yield must be equal to the CF presently on the market. Control of volatility losses of EPTC, butylate, and trifluralin in SE formulations have shown excellent weed control under delayed incorporation or no incorporation. Field trials with SE formulations of atrazine with metolachlor or alachlor with the addition of dicamba gave excellent control of a wide range of weed species equal to that of CF. In most cases crop yields from plots treated with SE formulations were equal or better than those obtained with CF under conventional and conservation tillage systems and on light and heavy soils.

Starch encapsulation has other uses such as facilitating formulations of microbial pesticides in sprayable or granular forms. A sprayable formulation of *Bacillus thuringiensis kurstaki* (Btk) increased its residual activity in simulated and field rainfall studies and showed efficacy similar to that of conventional chemical insecticides. Two granular types have been developed, one a conventional type which remains discrete through wet and dry periods, and an adherent type which slightly dissolves and remains stuck to a leaf surface even after drying.

Preparation of Controlled-Release Starch Encapsulated Pesticides: Advantages and Opportunities of Extrusion Processing

Merle E. Carr

Recent advances have been made in technology for encapsulation of pesticides within a starch matrix. This technology involves the entrapment of pesticides in the matrix without need for either crosslinking chemicals, ancillary polymers, or modification of the starch substrate. The latest technology utilizes extrusion compounding techniques to achieve the entrapment. Several types of solid, crystalline, and liquid pesticides have been successfully entrapped in unmodified cornstarch matrices by continuous, twin-screw extrusion processes developed at this Center. This report reviews and summarizes various aspects of the encapsulation research and development carried out over the past 3-4 years. Variables affecting the encapsulation efficiency and release rate properties of the products are discussed. The preparation, evaluation, and efficacy of starch encapsulated pesticides (herbicides) produced by a simulated scaled-up extrusion process and an engineering feasibility study for their large scale production will be reported by others.

Introduction

Starch has been investigated considerably as an entrapment matrix for a variety of pesticides prior to starch encapsulation by extrusion (1-10). Previous work has shown that starch controlled-release matrices can provide a number of benefits such as reduction in leaching, ground water contamination, toxicity, odor, volatility, and decomposition problems. The abundant availability, low cost, and physical nature of ordinary unmodified cornstarch in the United States is particularly attractive for such application. Other types of unmodified starches and flours are also suitable low-cost substrates for entrapment applications.

Various methods and procedures for incorporating pesticides into a starch matrix include the use of various types of natural and modified starches, crosslinking and/or coagulation chemicals, and combinations of starch with other polymers (1-4). Methods that have involved, for example, ionic and covalent crosslinking of starch xanthate, coagulation of alkali-treated starches with calcium chloride or boric acid, and formation of ionic or covalently bonded interpolymers can be effectively used. However, the most simple and cost-effective means of entrapment is by the natural process known as retrogradation (11). Starch retrogradation is the phenomenon by which gelatinized starch molecules in aqueous media reassociate and revert to water-insoluble aggregates through hydrogen bonding. Removal of water accelerates the bonding process and renders the starch essentially insoluble in water. The simplest procedure for incorporating a pesticide into a matrix of unmodified starch without other additives simply involves first, the aqueous gelatinization of the starch at about 90-95°C; secondly, incorporation of the pesticide into the expanded gelatinized starch matrix before any substantial extent of retrogradation occurs; thirdly, removal of water; and finally, particulating the dried matrix.

Various mechanical means have been used to form the starch encapsulated pesticides with limited processing flexibility, control, and efficiency. However, the most versatile, simple, and cost-effective means is by continuous twin-screw processing (12-17). Twin-screw extruders are well recognized in the food, feed, plastics, and rubber industries as highly efficient mixer reactors, particularly for high-solids and difficult mixing requirements. We have found the corotating, fully-intermeshing, twin-screw extruder to be ideal for encapsulating bioactive agents in unmodified starch matrices.

The purpose of the present report is to review and summarize starch extrusion encapsulation work carried out at this Center over the past 3-4 years. Variables such as temperature profile, screw design, screw speed, solids concentration, points of addition, additives, levels of addition, and other variables which can affect the matrix properties are discussed. The effect of these variables on encapsulation efficiency and rate at which herbicides are released from the matrix in aqueous media are presented.

Equipment

The entrapment of pesticides within a starch matrix was carried out using a ZSK 30 twin-screw extruder manufactured by Werner & Pfleiderer Corporation. The screws are corotating, fully intermeshing, and composed of numerous slip-on elements of various designs for

Carr is a Research Chemist, National Center for Agricultural Utilization Research, USDA-ARS, Peoria, IL 61604.

achieving desired feeding, conveying, and mixing capabilities and screw speeds from 50 to 500 revolutions/min (rpm). The processing section included 14 individual barrel sections (BS) having 7 zones and a die-head assembly (zone 8) to give a total L/D ratio of about 43:1 (12). All barrel sections were heated by electric units and cooled by a closed-loop chiller as called for by preset conditions on a remote control panel. The die-head assembly was also equipped with an electric heater and with various dies. Work was also carried out by replacing the die-head assembly with a die-face cutter (pelletizer) that can be fitted with various dies. Loss-in-weight feeders and high-pressure piston pumps were used for incorporating all materials into the extruder. A vacuum pump for removing water or volatiles has not been necessary in systems investigated to date.

Materials

A variety of starches, flours, meals, pesticides, pigment carriers, and surfactants have been used to prepare the starch encapsulated pesticide products by the ZSK 30 twin-screw extrusion processes. However, most of the work has involved the use of industrial-grade unmodified cornstarch because of its overall effectiveness, low cost, and ready availability.

Some 15 types of pesticides have been starch encapsulated by the ZSK 30 extrusion processes. However, most of the work has involved three widely-used herbicides. These include (1) granular atrazine, 6-chloro-*N*-ethyl-*N*-(methylethyl)-1,3,5-triazine-2,4-diamine, (2) liquid metolachlor, 2-chloro-*N*-(2-ethyl-6methylphenyl)-*N*-(2-methoxy-1-methylethyl) acetanilide, and (3) crystalline alachlor, 2-chloro-*N*-(2,6-diethylphenyl)-*N*(methoxymethyl) acetamide. Liquid "DUAL" and EPTC (S-ethyl dipropylthiocarbamate) were also evaluated considerably. Dual is actually 86% metolachlor active ingredient, containing a surfactant. Alachlor was incorporated as a liquid melt at 50°C.

Carriers that have been used to increase levels of active ingredients (a.i.) up to about 30% of the final product weight include Kaolin clay, Fullers Earth, diatomaceous earth products and silicates. The silicates were the most effective but the most expensive. Cost/performance aspects of the various carriers would require detailed consideration and study. In general, the use of carriers (absorbents) or surfactants have not been required unless about 15% or more oily-type herbicide is incorporated into the product. A solid such as atrazine can be well retained at high levels of incorporation without additives.

Procedures

A variety of procedures have been used, too extensive to present in detail in this report. However, some of the extrusion procedures are exemplified as follows.

Example 1
Starch (10% moisture) and atrazine were preblended and fed into barrel section number one (BS-1), and water was pumped into BS-3 using an intense mixing screw and a high temperature gelatinization profile. Barrel temperatures (°C) were set at 70 in zone number one (Z-1), 90(Z-2), 1OO(Z-3,4,5), 90(Z-6,7), and 90 (Z-8). Feed rates were such as to give various total solids concentrations from 36-75% and atrazine incorporation levels of 5-20% (final product weight basis after drying to about 10% moisture). Total feed rates ranged from about 7-14 kg/h. The material was extruded through the die-head opening (about 320 mm^2) using a screw speed of 400 rpm. A screw speed of 200 rpm was also used for the lower feed rates. In other work, the materials were extruded through dies with either four 2-mm-diameter holes or two 4-mm holes. Alternatively the die-head was replaced with a die face cutter using dies with hole diameters as small as 0.7 mm. The materials were dried, milled (pin mill), and sieved (generally 1.4-0.84 mm and 0.84-0.42 mm equal to 14-20 mesh and 20-40 mesh).

Example 2
Metolachlor or DUAL was pumped into BS-5 (starch at BS-1 and water at BS-3) using similar screw speeds, temperature profile, feed rates, and conditions as described above. In some instances, strands, at high solids concentrations, were chilled (BS-12,13,14) to reduce product expansion at the die; to prevent oil from exuding around the die holes when high levels of herbicide were used (15-25% active ingredient, final product basis); and to facilitate die face cutting.

Example 3
Various temperature profiles, screw configurations, screw speeds, and points of addition were used to feed either herbicide, absorbents, granular starch, or combinations of materials downstream (generally BS-7 to 10) following gelatinization of the starch upstream. Additional information is found in the discussion

sections.

Other Procedures

Procedures for determining encapsulation efficiency (EE), swellability, and release rate (RR) of the milled products have been reported (12-17). EE refers to the amount of herbicide retained by the granules after mild washing with chloroform as compared to the amount contained by the granules before washing (expressed as %EE). Unless specified, the amount retained before washing compared to the amount introduced into the gelatinized starch in the extruder was essentially quantitative. The extent to which the granules swelled when soaked in water for 24 h at 25-27°C is referred to as swellability. The rates at which the herbicides were released from the matrices in aqueous media at room temperatures while being swirled on an ORBIT SHAKER is referred to as release rate (RR). Product granules in early work were swirled in aqueous ethanol (90% water and 10% ethanol) to slightly facilitate the RR. Later in the procedure, only water was used.

Results and Discussion

Encapsulation efficiency (EE), swellability, release rate (RR), and ultimately the efficacy of the starch encapsulated pesticides can be affected to various extents by the types of materials, extrusion conditions, and ex-situ downstream processing conditions. These variables provide opportunity for preparing encapsulated products having a wide range of release characteristics. For example, the use of either unmodified, acid-modified, high-amylose, waxy (amylopectin), derivatized or other types of starches will each differently affect the physical properties of the matrix. Fillers, absorbents, and surfactants will further modify the properties. Extrusion conditions alone can importantly affect release characteristics of the products. For example, the use of a high screw speed and intense mixing screw can result in a relatively fast release product compared to a lower shear condition. Also, a partially gelatinized unmodified starch can effectively entrap levels of herbicide up to 10% resulting in a relatively fast release product compared to fully gelatinized starch. RR may also be affected by method, rate, and extent of drying the products. In general the RR will not be affected by drying the starch beyond about 14% moisture. One of the most important effects on RR is particle size of the milled products. Die-face pelletized particles would be expected to release more slowly than milled products of equal surface area, although not yet studied. The preferred method of ex-situ processing is continuous (1) die-face pelletizing to a desired particle size, (2) suspended conveying of the pellets in an enclosed stream of air, and (3) drying the pellets in a fluidized-bed dryer to about 12% starch moisture. Specific examples of variables that affect properties of the matrix are presented in the following sections.

Starch Concentration

Figure 1 shows that EE of the 2.03-0.84 mm (10-20 mesh) encapsulated atrazine products without a clay filler was not appreciably affected by processing the materials in the extruder at starch concentrations of 35-65% (starch/starch + water basis) and atrazine addition levels of 5-20%. Percentage of herbicide active agent (ingredient) refers to the amount contained by the product after drying to 10% moisture. Figure 2 shows that EE was very importantly affected at 65% starch concentration for the smaller 0.84-0.42 (20-40 mesh) particles as atrazine addition level was increased to 20% (62% EE).

Table 1 shows that increases in starch concentration (expressed as % solids) in the extruder from 35 to 65% very moderately reduced the EE of the starch encapsulated metolachlor, DUAL, and alachlor products, except for alachlor at 65% starch concentration. Reductions in EE was very significant for the 20-40 mesh products at 65% starch concentration. DUAL, which contained a surfactant, underwent the least reduction in EE at 65% starch concentration. It should be emphasized that essentially all the herbicide that was incorporated into the products by the extrusion process, was retained, and that EE refers to the retention of herbicide after chloroform washing.

In data not shown, the level at which liquid oily pesticides (or other oily materials such as corn oil, soybean oil, and mineral oil) could be incorporated into the gelatinized starch substrate was importantly related to the starch concentration. Less oil could be incorporated and retained by the matrix as the starch concentration in the extruder was increased.

The extent to which encapsulated products (unwashed granules) swelled when soaked in water is shown in Table 1 and Figure 3. Data show that swelling increased as starch concentration in the extruder was increased. This is believed to be due, to some extent, to shear-initiated breakdown of starch, particularly at 65% starch concentration. For a given level of oil

addition, the breakdown of starch at high solids can be reduced or eliminated by design, configuration, and speed of the screw.

The effect of starch concentration (% solids) on RR of starch encapsulated metolachlor, DUAL, and alachlor products (10% active ingredients, 10-20 mesh) in distilled water is shown in Table 2. The RR of the milled, unwashed products was affected less than might be anticipated based on differences in their swellability. Release was nearly complete in 21 h for metolachlor and DUAL. DUAL was released only slightly more quickly than metolachlor, whereas alachlor was released much more slowly (41-49% in 21 h).

Herbicide Addition Level

Figure 1 shows that atrazine addition level had a small effect on EE of the chloroform-washed granules. Disregarding the small effect of starch concentration in this case, the average EE values were 95, 92, and 88% for 5, 10, and 20% addition levels, respectively (2.03-0.84 mm equal 10-20 mesh products). In data not shown, EE of the washed metolachlor products decreased from 67% (10% addition) to 44% (20% addition).

For products prepared at 65% starch concentration, swellability increased with increased levels of atrazine (Figure 3) but decreased for increased levels of metolachlor (Table 3). This may be partially due to the relatively lower shear stress in the extruder that was encountered with use of metolachlor, resulting in minimal starch degradation.

Addition level of atrazine in products prepared at 65% starch concentration had little affect on RR of 0.84-0.42 mm (20-40 mesh) granules agitated in aqueous ethanol (Table 4). Table 5 shows that RR of the metolachlor products prepared at 65% starch concentration, was quite significantly greater for the 10% addition level compared to the 15-20% levels. To some extent, this may be due to the reduced shear stress effect on starch at the higher levels of oil addition. It should be pointed out that the RR test for the metolachlor products was carried out in water rather than aqueous 10% ethanol used in earlier work for atrazine products, so that direct comparisons of products cannot be made.

Screw Speed

Screw speed may importantly affect the matrix properties depending upon the extent of shear stress on the starch substrate. Variables such as starch concentration, type and addition level of herbicide, screw design/profile and other factors play an interacting role. An example of screw speed effect on the matrix is shown in Figure 4. Starch, clay (attapulgite), and atrazine were processed in the extruder using an intense mixing screw and normal gelatinization temperatures (90-95°C) at 200 and 400 rpm. Starch/clay ratio was 4:1; total solids concentration was 65%; and atrazine addition level was 10%. RR of both 1.4-0.84 mm and 0.84-0.42 mm (14-20 and 20-40) mesh products were considerably greater for a screw speed of 400 rpm than rates at 200 rpm. In data not shown, these differences were somewhat less pronounced as level of atrazine was decreased and the effect of the higher screw speed was much less for metolachlor due to its greater lubricity.

Temperature

Processing temperature can affect the matrix properties. In general, maximum level of loading can be achieved by fully gelatinizing the starch. Also completely gelatinized unmodified starch will undergo a greater extent of hydrogen bonding than partially gelatinized starch, resulting in a slower RR. Lower temperatures (e.g. 65-75°C) can be used to obtain a relatively fast RR. Various temperature profiles have been useful for special needs such as feeding materials downstream, cooling the material in order to decrease product expansion at the die, or pelletizing the material.

Feed Rate

Total feed rate can affect the properties of the matrix to various extents depending upon the net effect on the other variables such as mixing, shear, temperature, screw speed, and residence time. Thus, changes in feed rate may require adjustments in these and other variables such as screw design, die design, and L/D to offset effect of feed rate changes. Total feed rate (production rate) has been the least studied variable in using the ZSK 30 extruder. However, there has been indication that high levels of oily herbicide loading is more difficult to achieve at relatively high production rates.

Carrier Additives

The effect of various levels of clay (Fullers Earth) on EE (% entrapment) of starch encapsulated atrazine and metolachlor products is shown in Figure 5. The materials were processed using normal gelatinization temperature profile and an intense mixing screw at 200 rpm. The material was extruded through a 2x4-mm-diameter die. The herbicides were

quantitatively retained in the extrudate and milled after drying to 1.4-0.84 and 0.84-0.42 mm sizes (14-20 and 20-40 mesh) (10% active ingredients). The chloroform-washed atrazine products retained over 90% of the atrazine for starch/clay blends containing up to 40% clay. EE then decreased significantly as clay content was increased. EE for the metolachlor products was much less under the same conditions.

Figure 6 shows a straight line relationship between swell of particles (0.84-0.42 mm) in water and the percentage of clay in the blends of up to 80% clay. As expected the granules with the most clay swelled the least. In data not shown, the starch/clay granules with atrazine swelled slightly more than those with metolachlor.

The effect of clay in the matrix containing metolachlor (10%) had a surprisingly small effect on RR as exemplified by 1.4-0.84 mm (14-20 mesh) granules in Figure 7. When clay without starch was processed in the extruder at the same conditions as the starch/clay blends, the release of metolachlor was complete in 3 h compared to about 48 h for blends with 20-50% clay. Clay with only 10% metolachlor, but not processed in the extruder, released all of the herbicide in about 15 min.

In data not shown, RR of starch/clay extruded products containing 25% metolachlor was only slightly higher than those of the products containing 10% metolachlor. The RR was considerably greater for metolachlor than for atrazine at all levels of clay addition.

Other types of carriers such as diatomaceous earth, silicates, and ungelatinized granular starch have been used. Silicates were the most effective for obtaining high levels of oil loading (e.g., 20-25%). However, on a cost/performance basis the effectiveness of these materials need considerably more evaluation. Granular starch has been incorporated downstream and found to cause a 2 to 3-fold increase in RR.

Points of Addition

Points of addition at which starch, carriers, surfactants, and herbicide are incorporated into the extruder can play an important role in both maximum level of herbicide and RR that is obtained. For example, addition of high levels of oil directly after water addition may inhibit gelatinization of the starch even using high temperatures (100°C) and intense mixing screws. Although addition of the oil further downstream may allow starch to be gelatinized, the oil may not be completely retained due to insufficient residence time, even with intense mixing. The problem can usually be resolved by using a proper balance of parameters. Normally, points of addition are much less important for oil addition levels of up to about 10-12%. As another example, preblending of starch with a carrier vs. separate additions of the carrier at some point downstream can also affect loading and properties of the matrix. In general, the preferred procedures for optimization need a to be researched for each individual herbicide and extrusion system.

Other Variable

Other variables such as conditions of drying and testing the products and of method of jet cooking compared to extrusion cooking of starch for encapsulation of EPTC herbicide, has been reported previously in detail (15). Essentially, starch encapsulated EPTC products swelled slightly more in water after oven drying (50°C overnight) and released more quickly than air-dried products. Figure 8 shows that RR was dramatically increased by agitating (swirling) the particles using an orbital shaker compared to static conditions in water (15). Swirling at 300 gyrations/min released as much EPTC in 2 h as was released in 14 h at static conditions. The swirling method appeared to be a valid method for rapidly evaluating the products for RR. RR was on the order of 2 to 2.5 times greater for EPTC encapsulated by jet cooking than by extrusion.

Advantages

The use of a corotating, fully intermeshing, twin-screw extruder for encapsulating pesticides in a starch matrix offers several advantages over previous procedures investigated. The extrusion process utilizes conventional equipment readily adaptable to continuous encapsulation and ex-situ downstream processing. Processing techniques are relatively simple, versatile, efficient, and effective. Recent scale-up work on a ZSK 57 and a ZSK 58 at Werner & Pfleiderer has demonstrated that materials need not be preblended; can be extruded through dies with holes as small as 0.7 mm; can be pelletized at the die face; continuously conveyed to a fluidized bed dryer; and dried for direct packaging. Cost of the downstream processing, neglecting equipment cost, has been estimated to be less than one cent/lb of product. The use of unmodified starch (or flour), without need for chemicals, provides the most effective low-cost substrate available for the extrusion process and for obtaining a wide range of release characteristics. The major disadvantage is the

initial cost of extrusion equipment. However, high-production facilities should soon offset this initial investment in a successful operation.

References

1. Stout, E.I., B.S. Shasha, and W.M. Doane. 1979. Pilot plant process for starch xanthide encapsulated pesticides. Journal Applied Polymer Science 24:153.

2. Shasha, B.S., D. Trimnell, and F.H. Otey. 1981. Encapsulation of pesticides in starch-calcium adduct. Journal Polymer Science, Polymer Chemistry Edition 19.

3. Shasha, B.S. 1980. Starch and other polyols as encapsulating matrices for pesticides. *In* Controlled Release Technologies: Methods, Theory, and Application (Kydonieus, A.F., Ed), pp. 207-224. CRC Press, Inc., Boca Raton, FL.

4. Trimnell, D., B.S. Shasha, R.E. Wing, and F.H. Otey. 1982. Pesticide encapsulation using a starch-borate complex as the material. Journal Applied Polymer Science 27:3919.

5. Schreiber, M.M., B.S. Shasha, M.A. Ross, P.L. Orwick, and D.W. Edgecomb, Jr. 1984. Efficacy and rate of release of EPTC and butylate from starch encapsulated formulations under greenhouse conditions, Weed Science 26:679.

6. White, M.D., and M.M. Schreiber. 1984. Herbicidal activity of starch encapsulated trifluralin. Weed Science 32:387.

7. Wing, R.E., S. Maiti, and W.M. Doane. 1987. Effectiveness of jet-cooked pearl cornstarch as a controlled release matrix. Starch/Stärke 39:422.

8. Wing, R.E., S. Maiti, and W.M. Doane. 1988. Amylose content of starch controls the release of bioactive agents. Journal Controlled Release 7:33.

9. Schreiber, M.M., R.E. Wing, B.S. Shasha, and M.D. White. 1988. Bioactivity of controlled release formulations of starch-encapsulated EPTC, Journal Controlled Release 7:237.

10. Schoppet, M.J., T.J. Gish, and C.S. Helling. 1989. Effect of starch encapsulation on atrazine mobility in small undisturbed soil columns, (Proc. American Society Agricultural Engineering, New Orleans, LA, 1989), 1-13.

11. Doane, W.M., S. Maiti, and R.E. Wing. 1990. Encapsulation by entrapment within matrix of unmodified starch, U.S. Patent 4,911,952.

12. Carr, M.E., R.E. Wing, and W.M. Doane. 1991. Encapsulation of atrazine within a starch matrix by extrusion processing, Cereal Chemistry 68:262.

13. Carr, M.E., W.M. Doane, R.E. Wing, and E.B. Bagley. 1993. Starch encapsulation of biologically active agents by a continuous process, U.S. Patent 5,183,690.

14. Wing, R.E., M.E. Carr, D. Trimnell, and W.M. Doane. 1991. Comparison of steam injection cooking versus twin-screw extrusion of pearl cornstarch for encapsulation of chloroacetanilide herbicides, Journal Controlled Release 16:267.

15. Trimnell, D., R.E. Wing, M.E. Carr, and W.M. Doane. 1991. Encapsulation of EPTC in starch by twin-screw extrusion, Starch/Stärke 43:146.

16. Doane, W.M. 1993. Encapsulation of pesticides in starch by extrusion, Industrial Crops and Products 1:83.

17. Carr, M.E., R.E. Wing, and W.M. Doane. 1994. Clay as a carrier in starch encapsulation herbicide prepared by reactive extrusion, Starch/Stärke 46(1):9.

Table 1. Effect of starch solids during extrusion upon the encapsulation of metolachlor, Dual and alachior on properties of the matrices[1]

Product encapsulated	Solids (%)	10-20 Mesh Active agent (%) recovered[2]	10-20 Mesh Active agent (%) encapsulated[3]	20-40 Mesh Active agent (%) recovered[2]	20-40 Mesh Active agent (%) encapsulated[3]	Swellability in water[4] (%)
Metolachlor						
	35	97	92	98	89	150
	50	96	90	96	82	170
	65	96	86	95	69	180
Dual						
	35	98	92	98	90	160
	50	97	90	96	88	170
	65	96	86	95	83	190
Alachlor						
	30	98	90	97	85	200
	50	97	87	97	85	180
	65	97	72	96	68	360

[1]Starch feed was constant and water rate was 32 to 132 ml/min.

[2]Total active agent recovered in dry product

[3]Active agent remaining after washing dry product with chloroform.

[4]Sample (0.2 g) in water (4 ml).

Table 2. Effect of starch solids during extrusion upon rate of release of encapsulated metolachlor, Dual and alachlor into water[1]

Product encapsulated	Solids[2] (%)	% Released (h) 1	2	3	21
Metolachlor					
	35	27	38	49	90
	50	27	39	51	94
	65	26	43	53	100
Dual					
	35	27	40	52	95
	50	35	46	57	95
	65	39	54	65	97
Alachlor					
	35	11	20	23	49
	50	9	16	21	41
	65	11	18	23	46

[1]10-20 mesh unwashed samples (300 mg) in 70 ml water at 100 rpm.

[2]Starch/starch + water concentration in the extruder.

Table 3. Effect of metolachlor concentration during extrusion on properties of the matrices[1]

Metolachlor (%)	Metolachlor (%) 14-20 Mesh recovered	14-20 Mesh encapsulated	20-30 Mesh recovered	20-30 Mesh encapsulated	Swellability in water (%)
10	98	85	97	67	340
15	96	80	95	66	260
17.5	95	79	95	63	220
20	95	71	96	44	220

[1]Starch/starch + water concentration in the extruder = 50%.

Table 4. Release of atrazine from starch-encapsulated product in aqueous media[1]

Level of addition (%)	Atrazine encapsulated		Atrazine released: Percent			Atrazine released: (g/100g)[2]		
	(%)	(g/100g)[2]	(4 hr)	(24 hr)	(72 hr)	(4 hr)	(24 hr)	(72 hr)
5	94	4.7	21	29	32	1.0	1.4	1.5
10	87	8.7	20	30	41	1.7	1.6	3.6
20	61	12.2	18	29	35	2.2	3.5	4.3

[1]Cloroform-washed products (20-40 mesh) in aqueous 10% ethanol. (65% starch concentration).

[2]Of product.

Table 5. Effect of metolachlor concentration during extrusion upon the rate of release of metolachlor into water[1]

Metolachlor (%)	Percentage metolachlor released (h)			
	1	2	2	21
10	36	46	55	87
15	18	24	29	60
17.5	15	22	27	56
20	23	32	38	61

[1]14-20 mesh unwashed samples (300 mg) in 70 ml water at 100 rpm. Processed at 65% starch concentration.

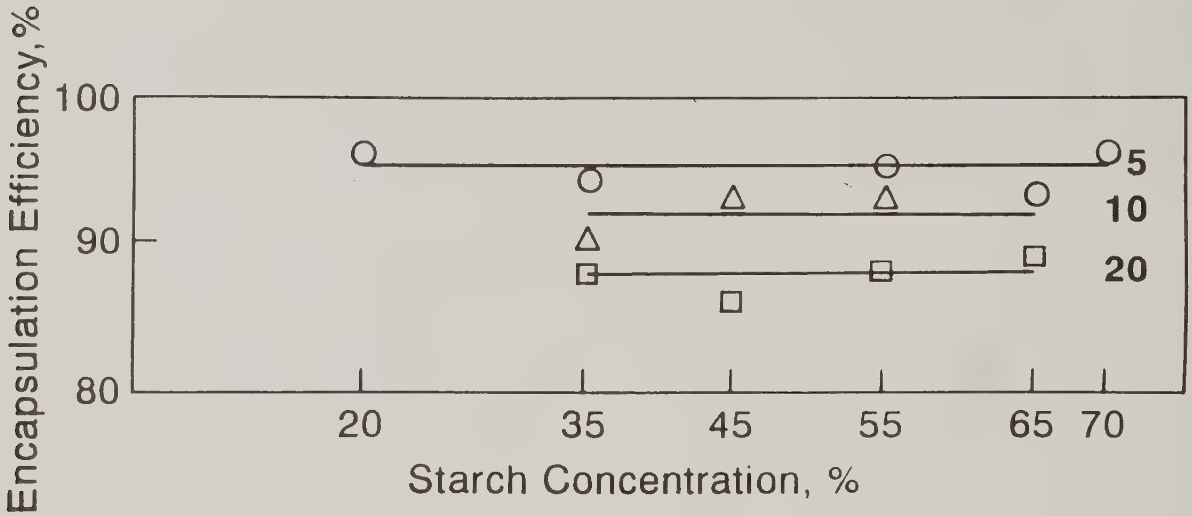

Figure 1. Efficiency of encapsulating atrazine in cornstarch matrices by extrusion processing (2.03-0.84 mm equal 10-20 mesh products). Atrazine addition levels were 5, 10, and 20% for products with 10% moisture.

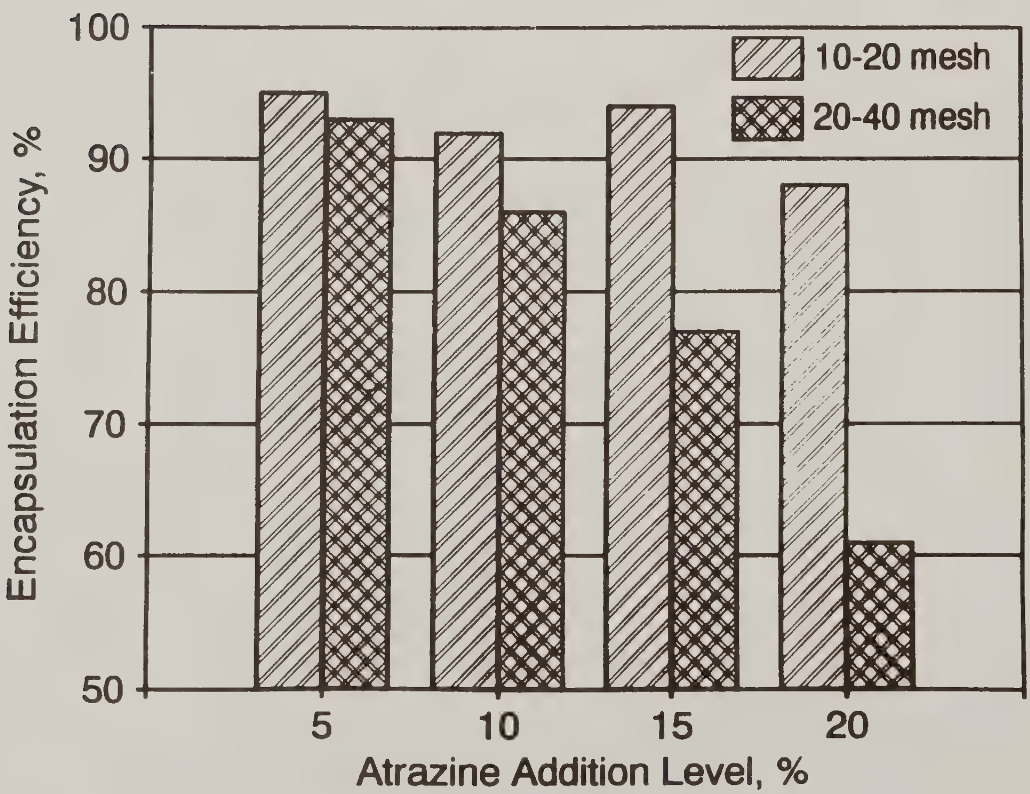

Figure 2. Effect of particle size and atrazine addition level on starch encapsulation efficiency.

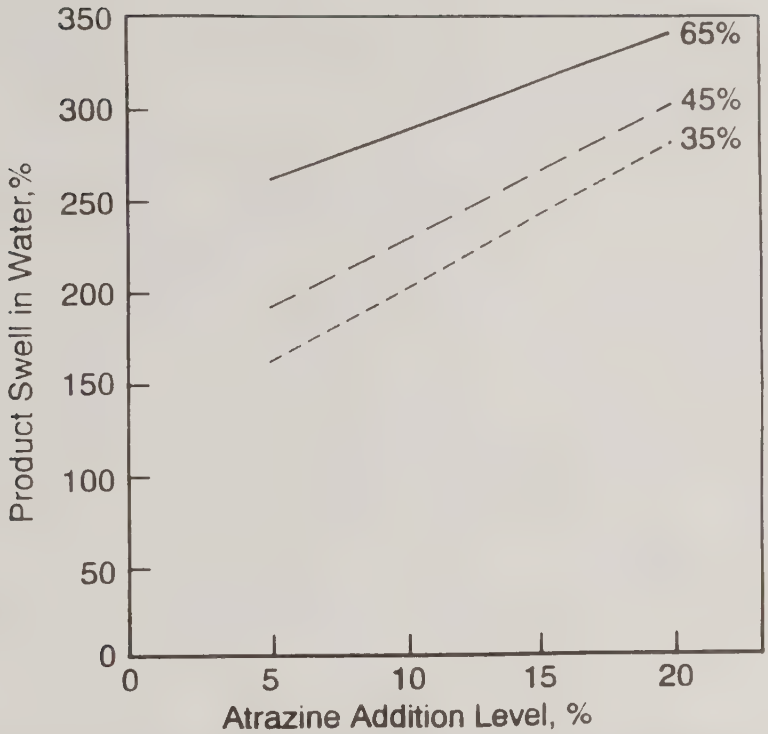

Figure 3. Effect of starch concentration (% solids) and atrazine addition level on swellability of starch-encapsulated products in water. Starch concentration in the extruder was 35-65%. Milled products (0.84-0.42 mm equal 20-40 mesh) were soaked in water at room temperatures.

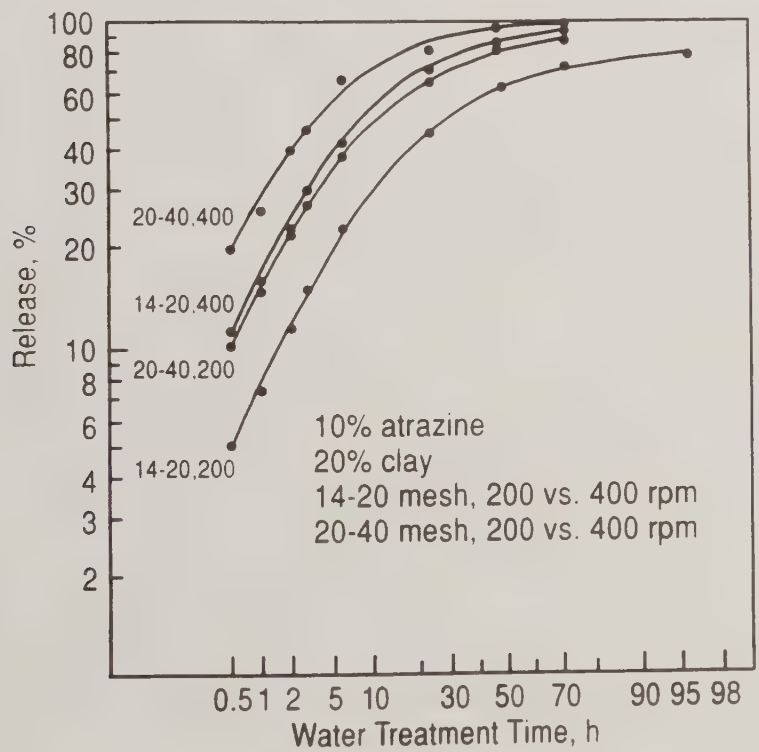

Figure 4. Effect of clay, particle size, and extruder screw speed on release rate (RR) of atrazine from encapsulated starch and starch/clay products.

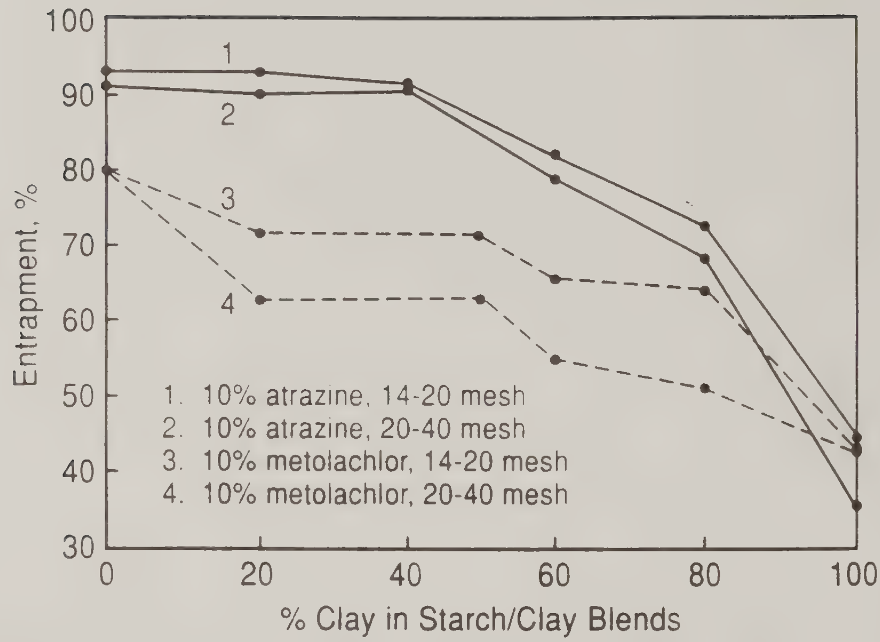

Figure 5. Effect of clay and particle size on efficiency of encapsulating herbicides in starch and starch/clay matrices by extrusion processing. Clay is Fullers Earth of 30/60 mesh.

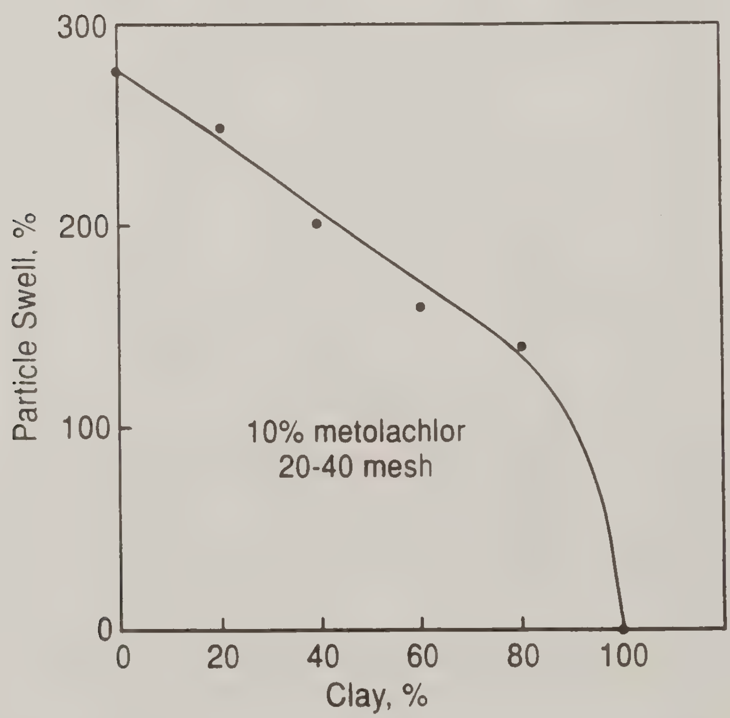

Figure 6. Effect of clay on swelling of starch- and starch/clay-encapsulated metolachlor products soaked in water for 24 h at room temperatures.

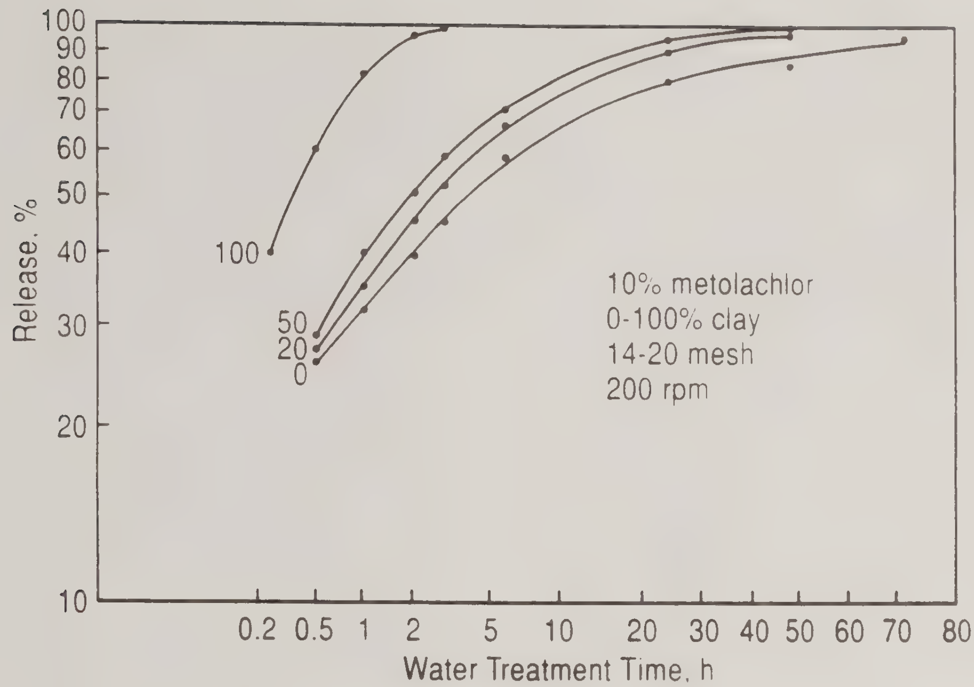

Figure 7. Release rates of metolachlor from starch- and starch/clay-encapsulated products. Particles were swirled in water for 24 h.

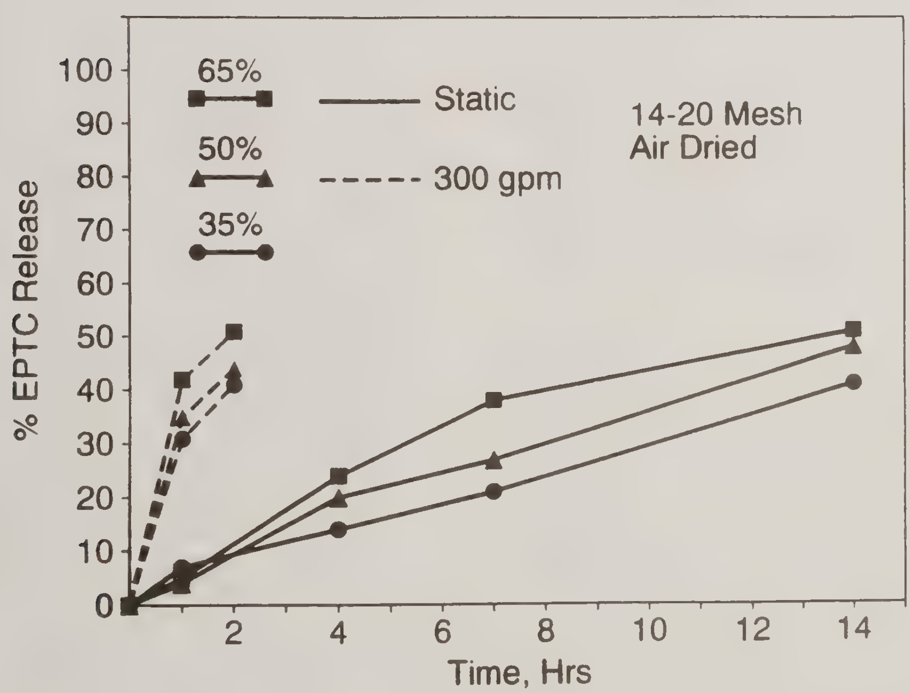

Figure 8. Effect of agitation on release rate of EPTC from starch encapsulated products.

Process Studies, Engineering Feasibility and Cost Analysis For Starch Encapsulation of Herbicides on the Co-Rotating Twin Screw Extruder

Joseph Grillo, Merle E. Carr, and Elisabeth Papazoglou

The co-rotating, fully intermeshing twin-screw extruder (ZSK) has been applied to the continuous compounding of starch encapsulated herbicide formulations. The ZSK is well recognized in the plastics, food and feed industries as a versatile mixer/reactor for the most difficult continuous processing requirements. Over the last 5 years, the continuous extrusion process for compounding bioactive agents into starch matrices has been developed. The continuous process of herbicide encapsulation includes the gelatinization of unmodified cornstarch in the extruder followed by the addition and incorporation of one or more active herbicides. The physical form of the herbicides ranges from oily liquid to powdery solid. This report will summarize the results of our process studies. Using our understanding of the various process interactions, a cost analysis will be presented for a scaled up commercial operation.

Introduction

Encapsulation of herbicides in starch is preferentially accomplished on the co-rotating fully intermeshing twin-screw extruder for a variety of reasons. Foremost is that continuous processing offers inherent economic advantage when compared to incumbent batch and fluidized bed processes. In addition, the twin-screw continuous process offers distinct process advantages. These include versatility in screw and process design, efficiency when changing over formulations, controlled mixing and product consistency.

Conversion of cornstarch and incorporation of bioactive ingredients characteristically includes the operations of starch hydration and gelatinization via the addition of water to cornstarch, incorporation of additives into the starch matrix, application of mechanical and thermal energy, followed by heat transfer with the onset of starch retrodegration and finally die forming. Overall process enthalpy is typically high depending on the concentration of water and the presence of other plasticizers. Quite conveniently, the twin screw is robustly designed for the most difficult continuous processing requirements (1) and can provide sufficient power without modification to the fundamental machine design. It is therefore well suited for a diverse range of customized starch encapsulation products.

Additionally, the twin-screw continuous process is flexible in process design due to its "building block" feature. The process section is composed of segmented units which can be pieced together and tailored to suit a unique set of process and mixing requirements. The advantages of the modular design include high degree of freedom in barrel arrangement and flexibility in altering the shear, mixing and residence time distribution. It is therefore possible to process a wide array of dissimilar formulations on a single unit.

Present work will first describe the experimental studies. Next, the results and characterizations of the twin screw process will be presented. The various process boundary conditions which have been identified will be described. Finally, we will present a model based on the observed boundary conditions and apply a cost analysis of the twin-screw process based on this model.

Theory

When encapsulating herbicide, the basic function of the extruder is to accept cornstarch, fully gelatinize it through a combination of mechanical and thermal energy, incorporate bioactive agent(s) and generate sufficient pressure to pass the processed matrix through a die. Figure 1 illustrates the twin screw process in terms of constituent operations. The initial task is to accept cornstarch into the feed throat, simultaneously convey and deaerate low bulk density powder, and move it in a positive direction. Solid active ingredients (a.i.) may be introduced along with cornstarch in the feed barrel. In this region, the extruder barrels are cold and the screw is configured with conveying elements which progressively decrease in pitch. Water is introduced into the system using a pressurized injection apparatus. The two components are mixed using a combination of dispersive and distributive kneading devices. The objective is to promote association between water and starch while eliminating any dry starch agglomerations which could become impermeable.

Liquid a.i. will usually be introduced directly following

Grillo is Senior Process Engineer, Werner & Pfleiderer Corp., Ramsey, NJ 07446. Carr is a Research Chemist, National Center for Agricultural Utilization Research, USDA-ARS, Peoria, IL 61604. Papazoglou is at FMC, Princeton, NJ 08543.

the water (prior to the onset of gelatinization) and be blended into the mixture using a distributive mechanism. In the case of chemically incompatible actives, incorporation is improved at high screw speed (high mixing intensity) while retention of starch structure and stable die forming are favored at low intensity conditions. In these cases, where opposing mixing criteria exist, optimums are sought and the application of experimental design is well suited.

Once all the ingredients have been introduced into the system, the task is to react the cornstarch with water to create a gel matrix structure which contains a dispersion of active agent. The physical nature of the dispersion, such as droplet size, influences functionality of the final product. The application of thermal and mechanical energy initiates the onset of structural change in the starch. The nature of these changes has been subject of numerous studies and has been recorded in the literature (2-4). Crystalline starch granules are disrupted and give way to a largely amorphous random polymeric melt. The water acts as a plasticizer to depress the glass transition temperature. Therefore, the minimum water concentration must be such that the matrix will melt below its decomposition temperature and yield a final product in which the polysaccharide forms a continuous polymeric phase. Starch transformations in this region are affected by extruder configuration, flow rate, temperatures, screw speed and moisture content of the starch.

The matrix is then prepared for discharge and die forming. This will involve adjustment in melt viscosity via heat transfer. Simultaneously, the cooled matrix will be pressurized for die forming. Both affects are sought in the same region of the extruder and the constituent operations are opposing. Therefore, optimization is required. The goal is to pressurize and discharge with minimal viscous dissipation such that the matrix is formable to the extent that hot face pelletizing at the die is possible via a high speed concentric type pelletizing system. In addition, the pellets should lack tackiness to the extent that they do not adhere together when contacted immediately after pelletizing. Related variables include flow rate, screw intensity - which is a combination of screw speed and element configuration, plasticizer concentration and die design. Die design considerations include number of holes for a given area, hole pattern, overall flow balance, land length (L/d) and material of construction. Hole diameter is usually determined by functional considerations in the end product and is not a design variable.

Overall, process optimization results when screw intensity is sufficient to create an amorphous melt and distribute active agent within the melt, but gentle enough to minimize heat generation which results from numerous sources of shear stress. Shear stresses encountered in the heat transfer, pressurization and die forming regions should be minimized in order to attain maximum flow rate. In addition, die restriction and pressure drop should be minimized for a given number of die holes and hole pattern - again, to minimize matrix heat generation.

Experimental

Process Configuration

Experiments were carried out on a Werner & Pfleiderer ZSK-57 twin-screw compounder. This extruder is intermediate in size and the data can be used as basis for scale up to commercial sized equipment. The process configuration is shown in Figure 2. The processing section consisted of 12 barrel segments with an L/d of 36:1. The cornstarch was typically metered into the first barrel while water was injected into the second barrel. The liquid a.i.'s were metered directly downstream of the water while the solid a.i.'s were metered into the feed barrel along with the cornstarch. Twin-screw gravimetric devices were used to meter the solid components while the liquids were metered using assemblies which consisted of a triplex piston pump, mass flow meter and pressure nozzles. Figure 3 shows a plan view of a 0.7 mm die plate. The hole pattern shown is typical of those used and illustrates our attempt to optimize open cross sectional area. The use of dies with hole diameters of 0.7, 1.0 and 1.5 mm are reported. The hole patterns were designed to yield the greatest number of holes for the available cross sectional area for minimum viscous dissipation yet on the other hand to allow for sufficient mechanical integrity to sustain operational die pressure. In addition, the holes were spaced out such that the pellets would not stick together upon cutting.

Discussion

The objective of all experiments was to identify the set of input process variables which allow for simultaneous maximization of certain responses. Input variables include screw design, screw velocity, barrel temperature set points, order of addition and die design. The primary response variables included, but were not limited to, upper flow rate limit, highest concentration of a.i., and smallest pellet size. Attainment of

maximum total flow rate and concentration of a.i. were considered most important since pellet size will vary for each product and set of application requirements. All three conditions - flow rate, a.i. concentration and pellet size - are directly opposing, and therefore, optimizations are again sought. We've identified the influencing variables and interactions which affect flow rate and concentration and will discuss each. Although we attempted to treat different herbicides "generically" as an additive, our initial experiments proved that such a generalization is not possible. Each system has its own unique process requirements. This uniqueness is not unexpected, since chemical structure, rheology and mechanism of action are different for each of the tested herbicides.

Results

Tables 1 and 2 list the herbicides that were processed. In all cases, these chemicals and formulations were commercially available, off-the-shelf compounds. None were formulated specifically for starch encapsulation or twin screw compounding. In addition to single active component formulations, numerous bioactive blends were encapsulated. These are listed in Table 2. Scanning electron microscopy was used to evaluate extent of gel formation and dispersion of active within the starch matrix. Table 3 summarizes the data and results for the various formulations. The data reported were attained at stable steady state conditions with acceptable gelatinization and dispersion. Efforts were concentrated on the DUAL system because it was one of the more difficult to incorporate at high levels due to its physical nature.

Order of addition of the a.i. was a critical variable when the active ingredient is an incompatible or semi-compatible (hydrophobic) oil. Both DUAL and corn oil were selected for this study. Corn oil was used as a placebo and is highly incompatible with the cornstarch system. Three distinctly different process limiting phenomena were observed. First, the oily a.i. tends to compete with water for association with starch and therefore inhibits the formation of a gel matrix. This becomes increasingly prominent at increasing output and a.i. concentration. In this case, the a.i. concentration limit can be offset by increasing water concentration. Next, chemical incompatibility limits maximum concentration. In this case, maximum incorporation required intensive mixing at high screw speed, which imparted heat to the matrix, thereby creating a heat transfer limitation at the die forming operation. Finally, the process was limited by rheological dissimilarities between matrix and oil. This phenomenon was studied by introducing a.i. at varying locations along the extruder barrel and observing the retention of oil in the discharged matrix. As extent of gelation increases prior to oil introduction, miscibility of a.i. into starch was reduced. At extreme conditions, two distinct phases of matrix and a.i. were noted at the discharge. In general, the optimum was achieved by a.i. addition prior to the onset of gelatinization, typically directly following water addition. It was also found that the use of compatibilizers such as surfactants and emulsifiers allowed increase in both rate and concentration when adding the oily a.i. upstream. This clearly suggests that each new system requires specific formulation design for compatibility with cornstarch.

In terms of process variables, the optimum range of screw speeds was between 150 and 300 min^{-1}. Two screw designs were ultimately chosen which balanced mixing intensity on one hand, and imparted minimum viscous dissipation. Figure 4 shows these designs. The first utilized conventional kneading blocks in the areas of starch gel formation and a.i. incorporation while the second utilized TME mixing elements in the regions corresponding to a.i. incorporation.

Several die plates were evaluated to determine the size of granules that could be generated using starch matrices (4). Table 4 presents data showing the effect of the number of holes and hole surface area in the die plate. Overall, total open cross sectional area is diminished as hole diameter is reduced. In comparing processing behavior as a function of die diameter, we observed that as die diameter was reduced and all other process variables were maintained constant, die discharge temperature increased. This increased temperature results in the earlier onset of a flow rate limit. This behavior is expected since the smaller die diameter will yield greater pressure drop which results in increased discharge temperature. This increased temperature results in the earlier onset of a flow rate limit.

Scale Up

Scale up of twin screw extrusion utilizes the data attained from the pilot extruder. For each herbicide system, the ultimate process rate limitation must be identified. The basic assumption is that the process will respond similarly on a larger extruder geometry. L/d is maintained constant and screw configuration is scaled up geometrically. If the assumption is correct, the

process can be "fine tuned" using extruder variables. Often, a new screw design must be evaluated and tested on the production-scale extruder. Potential process limitations include extruder volume, available power or heat transfer surface area. We observed that extruder volume and heat transfer area were the limiting factors for the tested herbicide/cornstarch matrices.

Volumetric scale-up is a cubic function of screw diameter as shown in equation (1).

$$G_{(target)}=G_{(model)}\cdot\frac{n_{(target)}}{n_{(model)}}\cdot\frac{D^3_{(target)}}{D^3_{(model)}} \qquad [1]$$

where G is flow rate, n is screw speed and D is screw diameter. Maintaining L/d, screw geometry and screw speed constant for a volumetric scale up produces equivalent degree-of-fill and average residence time if scale up is within the same family of extruders (target and model machine have equivalent geometrical clearances).

Heat transfer limited processes are scaled up according to inner barrel surface area as shown in equation (2).

$$G_{(target)}=G_{(model)}\cdot\frac{D^2_{(target)}}{D^2_{(model)}} \qquad [2]$$

All of the starch processes evaluated were not pure adiabatic systems. In most cases, direction of heat flow was from matrix to barrel surface. In this case, an overall heat transfer coefficient is calculated and then corrected for increased clearances between barrel wall and screw flight (larger screw diameter) and increased screw channel depth.

For the ZSK 57 pilot extruder model, a flow rate of 102.3 kg hr^{-1} was selected, based on a mean of all input data. The scale up factor from the 57 to the 177 mm extruder is 29.94, which yields a theoretical flow rate of 3046 kg hr^{-1} on the 177 mm extruder. The model process is scaled up according to a volumetric limit, since deviation from empirical heat transfer data can be corrected by adjusting L/d. The commercial system is shown in Figure 5. The design of this process allows for two a.i. feedstreams - a solid and liquid. Multicomponent formulations greater than two a.i.'s are possible but would require a pre-blending step. It was assumed that the starch would be supplied by p.d. railcar, solid a.i. in bulk bag and liquid a.i. in portable (250 gal) tanks. A 200 ton water-cooled chilling unit was calculated based on a process enthalpy of 0.175 kw-hr kg^{-1}. Specification of the fluidized dryer is based on a reduction in matrix moisture concentration from 20 to 10% and a reduction in matrix temperature from 93 to 27 °C using a specific heat (c_p) of 0.4 to 0.6 kcal kg^{-1} $°C^{-1}$.

Preliminary Cost-to-Make Estimate

A preliminary cost estimate for the production cost of a starch encapsulated herbicide indicates that for a hypothetical ZSK-177 with an annual capacity of 18.2 million kg of product, the conversion cost is \$ 0.0726 kg^{-1}.

The capacity was evaluated by scaling up the maximum production achieved on the ZSK-57 as explained previously. This resulted in 3046 kg hr^{-1}. Assuming operational capacity of 24 h day^{-1}, 250 day yr^{-1} we arrived at the estimated annual capacity of 18.2M kg of product. The rate of material loss was assumed 1%. The calculations also include 1.5 operators for 3 shifts per day, and capital of \$5,000,000. Maintenance costs are estimated at 2.5% of the invested capital. Energy requirements are scaled up from the 57 mm extruder and are estimated at 0.175 kw-hr kg^{-1} at a cost of \$0.06 $(kw\text{-}h)^{-1}$. We are able to estimate energy requirements because the SME (kw-hr kg^{-1}) remains constant when scaling up from pilot to production in the ZSK family of machines. We selected the highest SME value attained from all experiments to arrive at a conservative cost estimate of the production cost. The cost of \$0.06 (kw-$hr^{-1)}$ also accounts for all process power requirements. This brings the Total Operating Cost to about \$1.3M. Table 5 summarizes the cost estimation. The conversion cost is based on the total production output (does not include the material lost during start up or shut down).

The raw material cost depends on the type of product manufactured. Three scenarios were evaluated. Product A with a raw material cost of \$0.66 kg^{-1}, Product B with a cost of \$1.32 kg^{-1}, and Product C with a cost of \$2.2 kg^{-1}. The total production cost ranges therefore from \$0.739 kg^{-1} for Product A to \$2.30 kg^{-1} for Product C. The conversion cost is 3% of the raw material cost for Product C (expensive raw materials), and increases to 10% of the raw materials cost for Product C (the least expensive initial components).

Conclusions

The ability and versatility of encapsulating a wide range of herbicides in starch matrices using the twin-screw extruder has been demonstrated. The process boundary conditions, including output rate, optimum position for feeding additives and screw speed, have been determined via experimental design techniques. Attempts to generalize the process were not successful because there is no representative average of the various herbicide chemicals that are commercially available.

In incompatible or semi-compatible systems of starch-herbicide, order of addition was the most critical variable. In the same systems, a.i. concentration is limited by the chemical incompatibility with starch, the competition with water for starch association and the ability to die form the final product. Use of surfactants and emulsifiers greatly improved a.i. concentration and processability. However, a specific surface modification system needs to be developed for every herbicide formulation, particularly when high levels of incorporation are desired.

A Cost Analysis Estimate of the encapsulation process was generated based on scaling up the process from the 57 mm extruder. This evaluation suggests an encapsulation cost of \$0.0726 per kg of produced concentrate. The total production cost varies from \$0.739 kg^{-1} to \$2.295 kg^{-1} depending on the cost of the utilized raw materials.

References

1. Dreiblatt, A. Twin Screw Extruders, Process Plant Machinery, Butterworth, London (1989) 588 pp.
2. Mielcarek, D. Twin Screw Compounding. 1987. Chemical Engineering Prog. pp. 41-49.
3. Trimnell, D., R.E. Wing, M.E. Carr, and W.M. Doane. 1991. Encapsulation of EPTC in Starch by Twin Screw Extrusion. Starch 43:146.
4. Carr, M.E., R.E. Wing, and W.M. Doane. 1991. Encapsulation of Atrazine within a Starch Matrix by Extrusion Processing. Cereal Chemistry 68:262.
5. Wing, R.E., M.E. Carr, and W.M. Doane. Continuous Process for Starch Encapsulated Herbicides. Pesticide Formulations and Applications Systems 13 (1993).

Table 1. Bioactive ingredients

Common Name	Trade Name	Chemical Name
Alachlor	LASSO	2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide
Atrazine	many	6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine
Butylate	SUTAN	S-ethyl bis(2-methylpropyl)carbamothioate
Dicamba	BANVEL	3,6-dichloro-2-methoxybenzoic acid
EPTC	EPTAM ERADICAINE	S-ethyl dipropyl carbamothioate EPTC + dichlormid (2,2-dichloro-N-N-di-2-propenylacetamide)
Metolachlor	DUAL	2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide
Metribuzin	SENCOR LEXONE	4-amino-6-(1,1dimethylethyl)-3-(methylthio)-1,2,4triazine-5(4H)-one

Table 2. Bioactive Premixes

Trade Name	Common Name	Manufactuturer
SUTAZINE	Atrazine +Butylate	ICI Americas
none	Dicamba + Dual	-
none	Dicamba + Alachlor	-
none	Dicamba + Alachlor + Atrazine	-
none	Dicamba + DUAL+ Atrazin	-
BICEP	Metolachlor + Atrazine	CIBA-GEIGY
BULLET	Alachlor + Atrazine	Monsanto
none	Alachlor + Metribuzin	-

Table 3. Experimental Results When Using 1.0 & 0.7 mm Die Bores

Active Ingredient	Total Bioactive Concentration (%)	Water Concentration (%)	Total Rate (kg hr^{-1})
Atrazine	20	20	100
Metolachlor	10-22	15-20	110
Eradicaine	20	15	106
Sutazine	24.5	15	111
Dicamba + DUAL	18.5	15	103
Alachlor + Dicamba	41	15	103
Atrazine + Alachlor + Dicamba	21.8	15	108
Atrazine + DUAL + Dicamba	22	15	108
Atrazine + DUAL	14	16	98
Alachlor	9	17	92
Alachlor + Atrazine	13	16	97
Metribuzin	9	17	186
Corn Oil (placebo)	9	20	106

Table 4. Effect of Extruder Die Plate Configuration for Encapsulated Herbicides

Die Diameter(mm)	No. of Holes	Total Open Die Cross Section (mm^2)	Granule Size mm (mesh)
0.7	396	152	1(20)
1.0	308	242	2(10)
1.5	196	346	2.7(7)

Table 5. Encapsulated Herbicide Production Cost

Production rate (kg hr^{-1})	3,046		
Annual capacity (kg yr^{-1})	18,200,000		
Lost material rate (%)	1		
Annual depreciation ($ yr^{-1})	500,000		
Annual operator cost ($ yr^{-1})	154,440		
Annual maintenance cost ($ yr^{-1})	136,230		
Annual energy cost ($ yr^{-1})	357,500		
Indirect labor/overhead cost ($/yr)	150,000		
Total operating cost ($ kg^{-1})	2,855,974/yr		
Conversion cost ($ kg^{-1})	0.073		
	Product A	Product B	Product C
Raw material cost ($ kg^{-1})	0.660	1.320	2.20
Lost material ($ kg^{-1})	0.0066	0.0132	0.022
Raw material usage cost ($ kg^{-1})	0.739	1.406	2.295

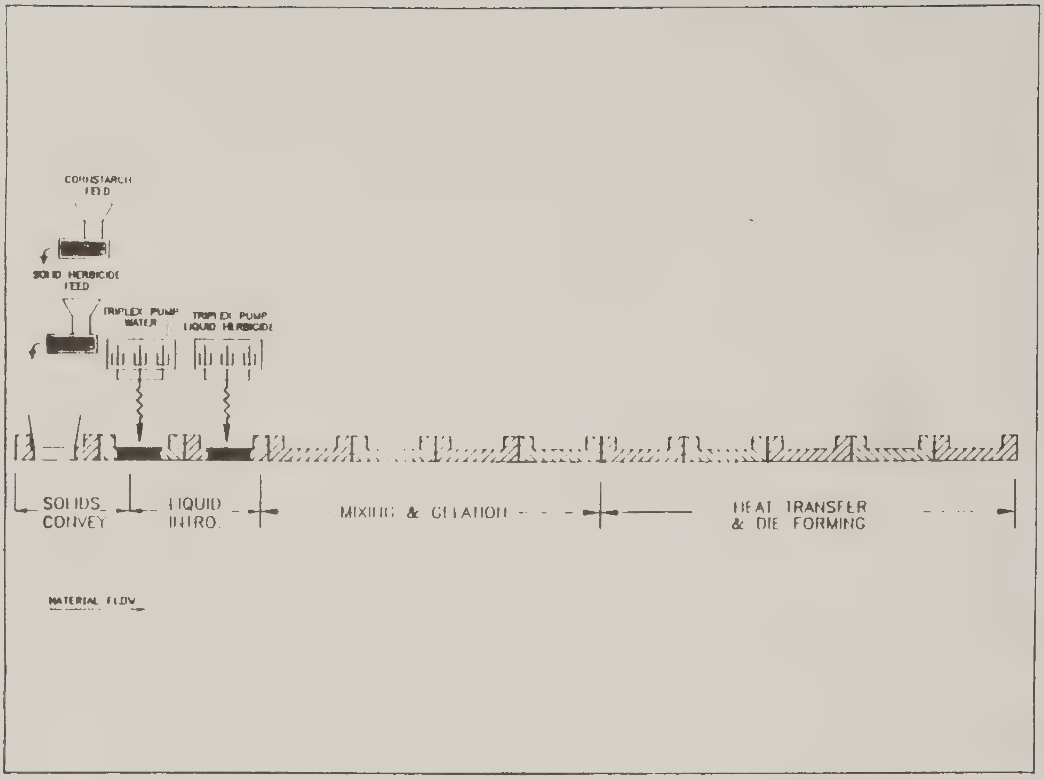

Figure 1. Constituent operations of a herbicide encapsulation in starch process on the twin screw extruder.

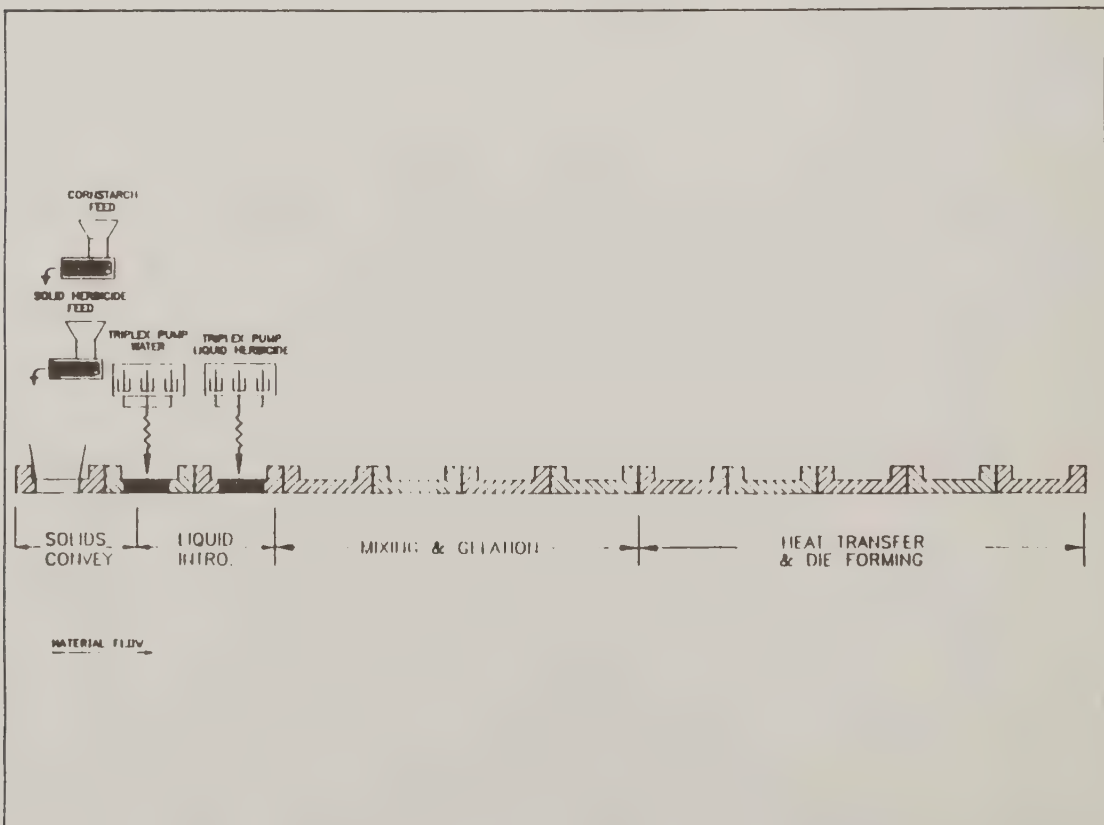

Figure 2. Flow diagram for the pilot 57 mm process.

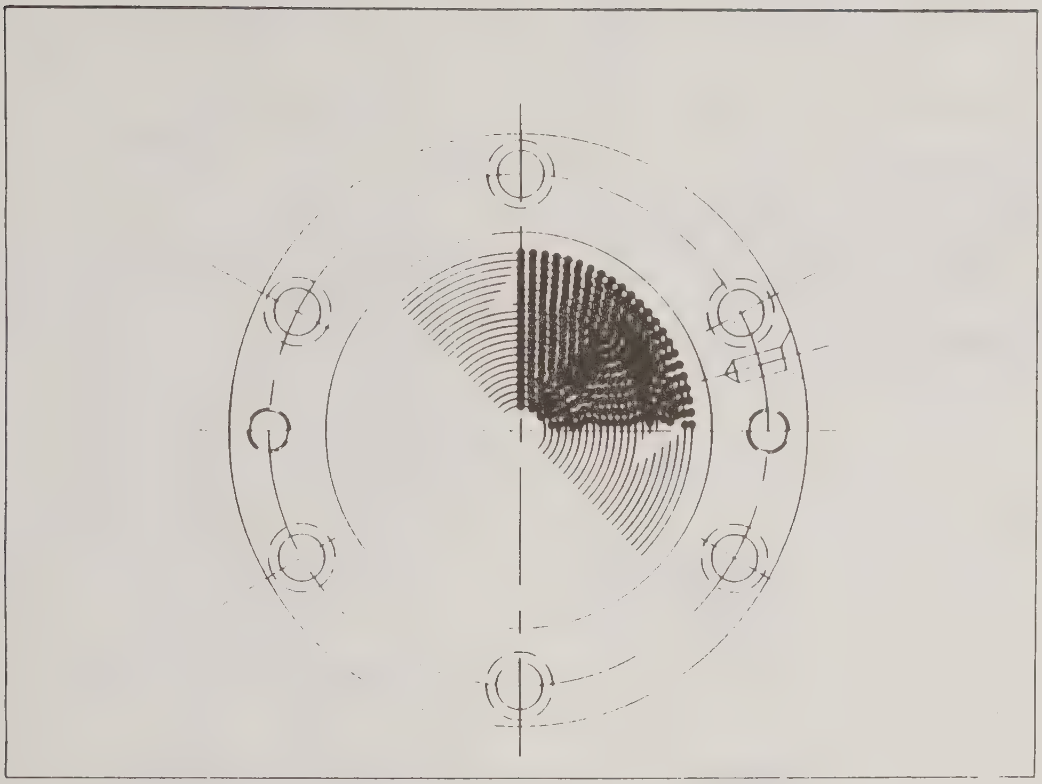

Figure 3. Plan view of 0.70 mm die plate.

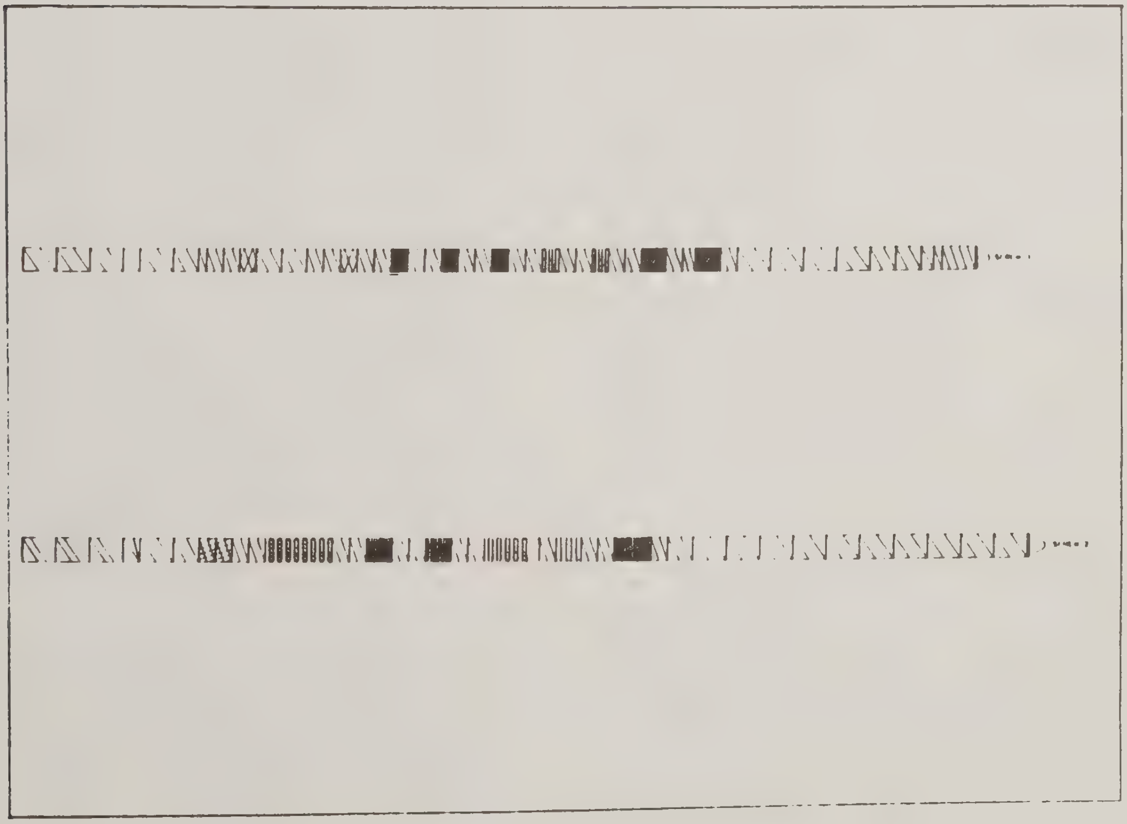

Figure 4. Screw configurations developed on the 57 mm extruder.

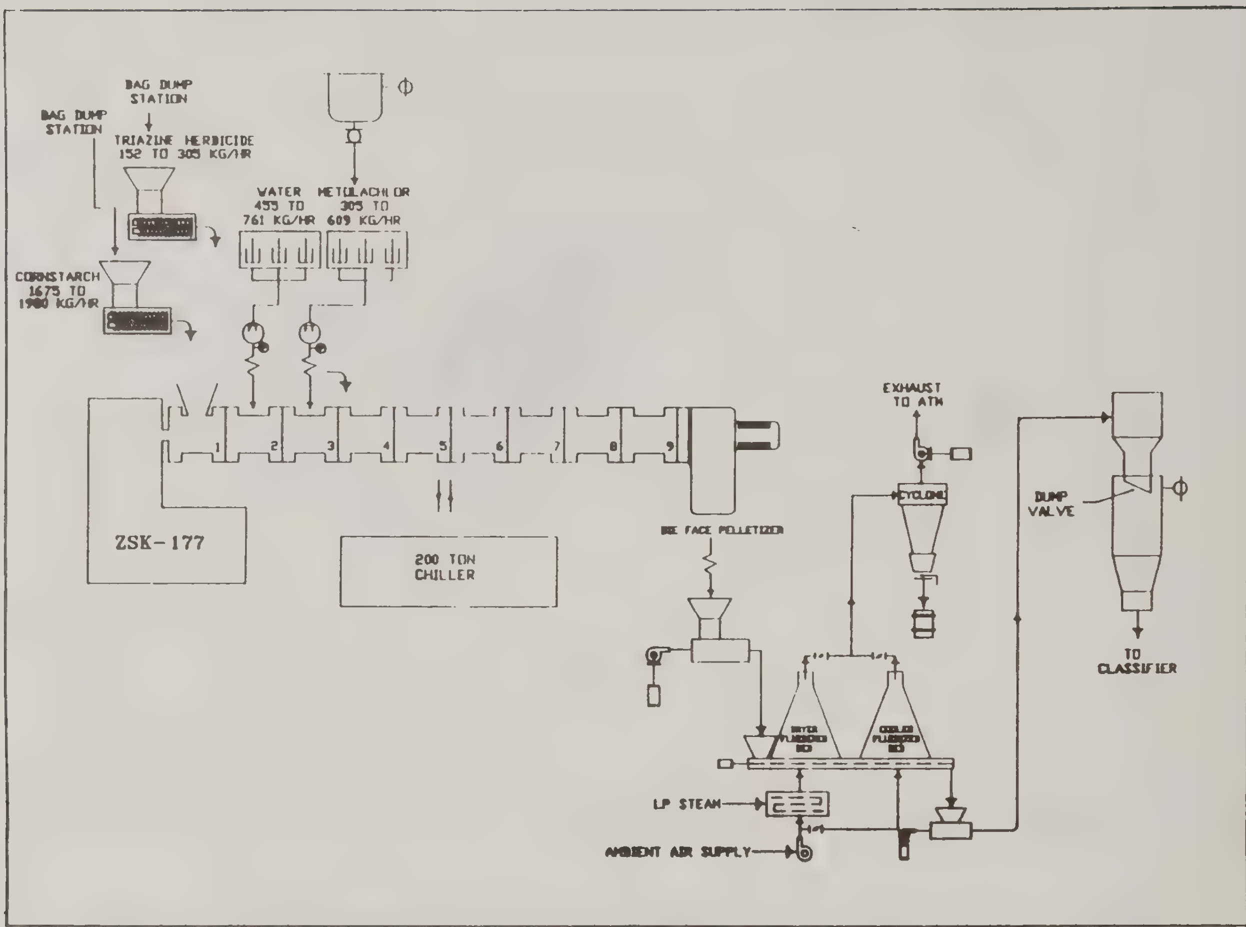

Figure 5. Commercial twin screw based facility - Process flow diagram.

Starch Encapsulated Controlled Release: Implications and Comparison with Commercial Formulations

Timothy J. Gish, Brian J. Weinhold, and Adel Shirmohammadi

Starch-encapsulation (SE) is an experimental controlled release technology designed to extend the period of time over which a herbicide is released into the soil environment. The objectives of controlled release are to improve efficacy and reduce negative environmental impacts. Relatively little is known about how various environmental factors influence rates-of-release, or how controlled release influences herbicide environmental fate. Laboratory and field studies were conducted to evaluate how environmental factors influence the release rate of SE-atrazine (2-choro-4-ethylamino-6-isopropylamino-*s*-triazine) and SE-alachlor (2-chloro-2',6'-diethyl-*N*-(methoxymethyl)-acetanilide). Decreasing water availability, significantly reduced swelling and subsequent rates-of-release for both herbicides. As starch granules imbibe water they swell, allowing the herbicide to diffuse more readily out of the granule. At 0 MPa, complete release of atrazine was observed after 21 days and after 7 days for alachlor. At -1.5 MPa, < 50% of the atrazine and < 80% of the alachlor was released from the starch granules after 28 days. Decreasing temperature also resulted in decreased rates of herbicide release. At 35°C nearly three times more atrazine and two times more alachlor were released than at 15°C. Soil microbial activity increased rates-of-release for both herbicides, likely the result of enzymatic breakdown of the starch matrix. After 21 days there was a twofold increase in atrazine release relative to sterile soil. Effect of microbes on alachlor release was apparent only at early times. After 5 days there was a 20% increase in alachlor release compared to sterile soil. The enhanced release of alachlor relative to atrazine under varied environmental conditions was attributed to alachlor's greater solubility in water. Controlled release of atrazine reduced mobility and volatility relative to commercial formulation (CF). Although the SE-formulations are experimental, modification of herbicide behavior was observed that could reduce negative environmental impacts.

Gish is a soil scientist, Hydrology Lab., USDA-ARS, Beltsville, MD 20705. Wienhold is a soil scientist, Northern Great Plains Research Lab., USDA-ARS, Mandan, ND 58554. Shirmohammadi is Assoc. Prof., Dept. of Agri. Engr., Univ. of Maryland, College Park, MD 20742.

Optimization studies based on herbicide characteristics should help maximize herbicide performance.

Introduction

Over the past three decades, polymer chemists and soil scientists have been developing controlled release formulations of pesticides for agricultural use. The main rationale for controlled release pesticide formulations has been to increase efficacy; however, with increased interest in environmental quality, controlled release pesticide formulations are also being evaluated for their ability to reduce environmental contamination.

Determination of pesticide environmental impact is complex, and to a large extent is governed by how the pesticide is partitioned between the adsorbed, liquid and air phases. Adsorbed pesticides can be transported in runoff to surface waters (1) or transported preferentially to shallow groundwater through void root channels or soil cracks in a colloidal suspension (2). On the other hand, wet, warm soils have a propensity to favor vapor loss to the atmosphere (3). Additionally, the timing of precipitation events also effects environmental fate of herbicides (2, 4). Rainfall occurring shortly after application can result in significant preferential transport of pesticide to shallow groundwater.

Starch-encapsulated (SE) pesticides maintain a rate-limited release of the pesticide, limiting the amount of pesticide available for transport at any given time. Release of a SE compound is governed mainly by a diffusion process (5). When starch granules are applied to the soil they imbibe water, swell and the encapsulated compound diffuses out of the starch matrix. A strong correlation has been shown to exist between the degree of swelling exhibited by starch granules and the rate of release of an encapsulated herbicide (6). Factors influencing rate of release from the starch granules can be placed into one-of-three categories; granule characteristics, characteristics of the encapsulated chemical, and environmental conditions.

Characteristics of the granule include granule size (7), type of starch used (amylose to amylopectin ratio) (8), agent used to crosslink the starch molecules, and amount of pesticide present in the granule (9). Granule size effects the surface-to-volume ratio and, therefore, the distance the chemical has to diffuse in order to leave the granule. Small granules exhibit faster rates of release than do larger granules (10). Granule composition (type of starch and crosslinking agent)

indirectly effects pesticide rate of release by modifying the degree of granule swelling that occurs in the presence of water. Wing, et al. (8) reported that as the percentage of amylose in the starch granules increased, the degree of swelling exhibited by the granules declined and the rate of release of the encapsulated chemical also declined. Borate starch granules (granules prepared using borate to crosslink starch xanthate macromolecules) swell to a greater degree than do jet cooked starch granules. This results in faster release of the encapsulated chemical. Release of atrazine from borate starch granules was essentially complete after four days compared to eight days for complete release from two jet cooked formulations (11). Finally, the rate of release also increases, as the amount of chemical encapsulated in the granule increases (9).

This paper reviews the environmental factors influencing rate-of-release of atrazine and alachlor from starch granules. The effect of this controlled release process on herbicide behavior will be compared to commercial formulation (CF) herbicide behavior by assessing field-scale mobility and volatilization.

Environmental Factors Influencing Release

Environmental factors effect herbicide rates of release from starch granules by influencing either diffusion mechanics or by altering the integrity of the starch granule. Common environmental variables include water availability, temperature and microbial activity. Water availability may exert an influence on herbicide release by controlling water uptake by the granule which determines granule swelling and subsequent herbicide release. Soil temperature may effect granule swelling as well as diffusion mechanics. The starch granules are also biodegradable, and as such are subject to decomposition and subsequent release of the herbicide.

Water Availability

The water potential is one measurement of the availability of soil water. As water is lost through evapotranspiration, a larger portion of the soil water becomes bound to colloids. The decline in soil water content leaves less unbound water so the energy status of the water, the soil water potential, declines. Polyethylene glycol (PEG) has been used to simulate a reduction in soil water potential (6, 12). The hydrated PEG molecule is very large and is unable to enter the pores of the starch granules, leaving only unbound water in the PEG solution to enter the starch matrix. When starch granules were placed in solutions of decreasing water potential, swelling and release of atrazine and alachlor declined as water potential declined (Figure 1). Additionally, alachlor release was more rapid than atrazine. After 5 days, 87% percent of the alachlor was released in a -0.5 MPa solution, while atrazine release in a -0.5 MPa solution was only 73% after 28 days. The enhanced release of alachlor was attributed to alachlor's greater solubility in water (240 mg L^{-1}) than atrazine (33 mg L^{-1}).

Rainfall events and subsequent evapotranspiration will generate several wetting-drying cycles over the growing season. The greatest differential in water availability should be at the soil-atmosphere interface, where the starch granules reside. As a result, redistribution of water after a rain event may draw the herbicide into small soil pores where rapid transport is less likely. Although there is no commercial instrumentation that can effectively monitor water potentials near the soil-atmospheric interface, the laboratory studies indicate that soils with greater water retention will be more effective in maintaining high release rates than a sandy soil. It also suggests that atrazine release will be less effective when subjected to drought conditions.

Temperature

Since diffusion is defined as the random thermal motion of molecules, an increase in temperature will also influence diffusion. Temperature has been shown to increase herbicide rates of release from the starch granules (6). At 35°C nearly three times more atrazine and two times more alachlor was released from starch granules than at 15°C at all sampling times (Figure 2). At 35°C and a water potential of 0 MPa complete release of atrazine occurred after 8 days while at a water potential of -1.0 MPa only 30% of the encapsulated atrazine had been released from the starch matrix after 8 days. At 35°C and a water potential of 0 MPa complete release of alachlor occurred after 1 day while at a water potential of -1.0 MPa release of alachlor was not complete after 8 days.

In the spring, when most crops are planted, soil surface temperatures vary depending on moisture status, plant cover and the amount of surface residue. The results discussed above suggest that release of SE herbicides applied to cool, dry soil will be very slow compared to release of SE herbicides applied to warm, moist soil.

Soil Microbial Activity

Soil microbes are able to produce the enzyme amylase which catalyzes the breakdown of starch. Through this

process the microbes are able to utilize starch as an energy source. It seems reasonable to assume that microbial activity around a starch granule will result in granule decomposition and increased release of the encapsulated herbicide (6). Schreiber et al. (13) observed microbial activity in the vicinity of soil applied starch granules and Trimnell et al. (10) reported increased release of trifluralin when starch granules were added to solutions containing amylase. Soil microbial activity significantly increased the rate of release of atrazine and alachlor from starch granules applied to non-sterile soil compared to granules applied to sterile soil (Figure 3) (6). After 28 days, more than 90% of the encapsulated atrazine was released when incubated in non-sterile soil, compared to < 70% in sterile soils. The effect of microbial activity was less pronounced on alachlor largely because alachlor is released so quickly microbial activity had a short time period to effect release.

Effect of Controlled Release on Environmental Fate

Mobility and Persistence

Most herbicides have a high affinity for the soil matrix and are adsorbed quickly. However, a portion of the applied herbicides can move preferentially, posing a risk to groundwater contamination. Since preferential transport is a convective process, increasing the role of diffusion may decrease mobility.

The leaching potential for herbicides is greatest immediately after application, when herbicide concentrations are the greatest and plant evapotranspiration is negligible. Field-average atrazine residue levels > 240 $\mu g\ L^{-1}$ at ~ 1m have been observed a few days after application, a consequence of preferential transport (4, 14). To evaluate the effect of SE on herbicide transport, a laboratory experiment was conducted using small soil cores extracted from a no-tillage field. Forty soil cores were subjected to water inputs that simulated preferential flow conditions and effluent collected so that transport of technical grade atrazine and three experimental SE formulations could be compared (14). After 16 pore volumes > 35% of the technical atrazine had leached through the small cores compared to 1-10% for the three SE formulations. Although the duration of this latter study was < 1 month, it was an indication that SE atrazine would be less susceptible to rapid transport during the same time it has the greatest leaching potential. This study also served as justification for evaluating field-scale behavior of SE herbicides.

In a two year field study, the mobility and persistence of SE and CF atrazine were compared in adjacent 0.25 ha fields (15). Persistence of SE herbicides was greater than CF (Figure 4). Increased persistence was due not only to the gradual release of herbicide over time, but the manner in which it was released. After 151 days in 1990, and 161 days in 1991, greater than ≈ 36% of the atrazine applied as SE was in the top 5-cm increment while less than 1% of the atrazine applied as CF was recovered in the top 1.1 m of soil (Figure 5). No difference between SE and CF alachlor mobility was observed (Figure 6).

Increased SE atrazine persistence is likely due to controlled release from the starch granule and its dependence on soil water availability. During a rain event, only a fraction of the applied SE atrazine is available for transport while all of the commercial applied broadcast spray may be transported in solution or colloidal suspension. In addition, after the rain event has ceased, a portion of the CF atrazine may be preferentially located along the walls of void root channels and soil cracks, susceptible to further movement from subsequent rain events. Subjected to the same meteorological conditions, only a fraction of the SE-atrazine will be available for transport. After the rain has ceased, the soil water potential of the soil surface will be large, maximizing release from the starch granules. The concentration gradient around the granule should also be larger resulting in enhanced diffusive movement into the soil matrix (Figure 7). As the soil dries out, atrazine rate of release decreases. Since large soil pores will empty first, water will move into successively smaller pores, carrying pesticide into smaller pores that are less susceptible to preferential flow mechanics resulting from subsequent rain events. The difference between SE and CF mobility is largely due to the smaller flow pathways utilized with SE.

Volatilization

Volatilization is one of the major loss pathways for some pesticides. Pesticide present in the vapor phase in the atmosphere may contaminate surface water by washout in precipitation, fallout of particulate material to which the pesticide has become adsorbed, and by direct exchange between the atmosphere and water surface. Glotfelty et al. (16) estimated that atrazine entering the Chesapeake Bay in washout and fallout was about 10% of that entering the bay in runoff. Based on atmospheric and surface water concentrations of atrazine, and the distribution coefficient between air and water for atrazine they also determined that the Chesapeake Bay was undersaturated and the net flux of

atrazine should be from the atmosphere to the bay. However, they were unable to determine the magnitude of this flux.

A number of studies utilizing SE herbicides have demonstrated increased efficacy when compared to commercial formulations (17-19). The increase in efficacy of SE herbicides was attributed to reduced volatilization. However, these studies did not report any measured volatilization rates, but inferred it from pesticide dissipation. Unfortunately, there are a number of loss pathways that effect pesticide dissipation (volatilization, chemical, biological and photo-degradation, leaching, and plant uptake) thereby generating some speculation as to the impact of SE on volatility.

In a greenhouse study, volatilization of atrazine and alachlor applied as either SE or CF was compared at three temperatures (15, 25, and 35°C) (20). Cumulative volatilization of CF atrazine at 35°C was nearly two orders of magnitude greater than at 15°C (Figure 8). Cumulative volatilization of CF atrazine was approximately four times that of SE atrazine at all temperatures. The effect of SE on volatilization of alachlor was opposite that of atrazine. At 25 and 35°C volatilization of SE alachlor was two fold greater than for CF alachlor (Figure 9). These results suggest that the effect of SE on pesticide volatilization are dependent on the chemical characteristics of the encapsulated pesticide. When starch granules are applied to a moist soil surface they imbibe water and the encapsulated chemical goes into solution within the starch granule where adsorption of the chemical by the matrix is low. For atrazine, the solution concentration within the granule likely remains low due to its low solubility in water (33 mg L^{-1}), which combined with it's low Henry's Law constant (2.5×10^{-7}), results in little volatilization. In contrast, the solution concentration of alachlor within the granule may be an order of magnitude greater (solubility 240 mg L^{-1}) than that of atrazine resulting in a much steeper solution concentration-vapor density gradient for alachlor than for atrazine. This steep gradient, combined with alachlor's higher Henry's Law constant (1.3×10^{-6}), results in much greater volatilization.

Volatilization of atrazine and alachlor under conventional and no-tillage may be different due to localized differences in temperature, organic matter content, and water content. Additionally, tillage practices affect pesticide behavior by altering biological activity, and evaporation (21-24). Consequently no-tillage practices frequently require higher applications to maintain yields (25). Recently, Wienhold and Gish (26) evaluated volatilization of SE and CF atrazine and alachlor on established conventional and no-tillage fields (Figure 10). After 35 days, cumulative volatilization of atrazine was < 2% of that applied to both tillage practices. For CF atrazine, 9% volatilized from conventional tillage while only 4% was volatilized under no-tillage. The lowest alachlor volatilization losses were also with the starch encapsulated formulation under no-tillage. Both CF and SE alachlor volatilization were high (13 and 14% of that applied, respectively) under conventional tillage. The lower volatilization losses under no-tillage were a result of several small rain events that occurred within the first 5 days of application which appear to wash the herbicides below the plant litter. Additionally, weed control was equal to or greater than that observed with the commercial formulation over the three years evaluated.

Conclusions

Starch encapsulation is a controlled release technology that shows potential for modifying the behavior of pesticides. The influence SE has on pesticide behavior appears to be variable, depending largely on the characteristics of the encapsulated chemical. Starch encapsulation modifies the behavior of a chemical by controlling the rate the chemical is released into the environment. Rate of release is strongly influenced by environmental factors, especially soil water availability and temperature, and characteristics of the encapsulated chemical, especially solubility in water. Mobility of SE atrazine and alachlor, both runoff and leaching, was reduced compared to that of CF atrazine and alachlor. Persistence of SE atrazine was substantially greater than that of CF atrazine. This increase in persistence was likely due to reduced losses of atrazine to leaching, and volatilization. Persistence of alachlor was not influenced by SE, likely because of the rapid rate of release for alachlor. Compared to CF, volatilization of SE-atrazine was dramatically reduced in greenhouse and field experiments. The effect of SE on volatilization of surface applied SE alachlor is highly dependent on tillage practice, being greater under conventional tillage. These results suggest that SE technology may be a useful approach for reducing environmental contamination by agriculturally applied pesticides, especially under no-tillage practices.

References

1. Glotfelty, D.E., A.W. Taylor, A.R. Isensee, R. Jersey, and S. Glen. 1984. Atrazine and simazine movement to Wye River Estuary. J. Environ. Qual. 13:115-121.

2. Gish, T.J., A.R. Isensee, R.G. Nash, and C.S. Helling. 1991. Impact of pesticides on shallow groundwater quality. Trans. Am. Soc. Ag. Eng. 34:1745-1753.

3. Spencer, W.F., W.J. Farmer, and M.M. Claith. 1973. Pesticide volatilization. Res. Rev. 49:1-47.

4. Isensee, A.R., R.G. Nash, and C.S. Helling. 1990. Effect of conventional vs. no-tillage on pesticide leaching to shallow groundwater. J. Environ. Qual. 19:434-440.

5. Schreiber, M.M., and M.D. White. 1980. Granule structure and rate of release with starch-encapsulated thiocarbamates. Weed Sci. 28:685-690.

6. Wienhold, B.J., and T.J. Gish. 1992. Effect of water potential, temperature and soil microbial activity on release of starch encapsulated atrazine and alachlor. J. Environ. Qual. 21:382-386.

7. Trimnell, D., and B.S. Shasha. 1990. Controlled release formulations of atrazine in starch for potential reduction of groundwater pollution. J. Controlled Release 12:251-256.

8. Wing, R.E., S. Maita, and W.M. Doane. 1988. Amylose content of starch controls the release of encapsulated bioactive agents. J. Controlled Release 5:79-89.

9. Carr, M.E., R.E. Wing, and W.M. Doane. 1991. Encapsulation of atrazine within a starch matrix by extrusion processing. Cereal Chem. 68:362-266.

10. Trimnell, D., B.S. Shasha, and F.H. Otey. 1985. The effect of α-amylases upon the release of trifluralin encapsulated in starch. J. Controlled Release 1:183-190.

11. Gish, T.J., B.J. Wienhold, and A. Shirmohammadi. 1993. Effect of starch-encapsulation on behavior of atrazine and alachlor. Am. Inst. Hydro. Proceedings of the Joint CIS/USA Hydrogeology and Hydrology Mt., May 6-8, 1993. Washington D.C. 109-124.

12. Zur, B. 1966. Osmotic control of the matric soil-water potential: I. Soil-water system. Soil Sci. 102:394-398.

13. Schreiber, M.M., M.D. White, R.E. Wing, D. Trimnell, and B.S. Shasha. 1988. Bioactivity of controlled release formulations of starch-encapsulated EPTC. J. Controlled Release 7:237-242.

14. Gish, T.J., M.J. Schoppet, C.S. Helling, A. Shirmohammadi, M.M. Schreiber, and R.E. Wing. 1991. Transport comparison of technical grade and starch-encapsulated atrazine. Trans. ASAE 34:1738-1744.

15. Gish, T.J., A. Shirmohammadi, and B.J. Wienhold. 1994. Field-scale mobility and persistence of commercial and starch-encapsulated atrazine and alachlor. J. Environ. Qual. 23:355-359.

16. Glotfelty, D.E., G.H. Williams, H.P. Freeman, and M.M Leech. 1990. Regional atmospheric transport and deposition of pesticides in Maryland. In: D. A. Kurtz (ed.) Long Range Transport of Pesticides. Lewis Publ. Inc. Chelsea, MI. 199-221.

17. Schrieber, M.M., B.S. Shasha, M A. Ross, P.L. Orwick, and D.W. Edgecomb Jr. 1978. Efficacy and rate of release of EPTC and butylate from starch encapsulated formulations under greenhouse conditions. Weed Sci. 26:679-686.

18. Coffman, C.B., and W.A. Genter. 1980. Persistence of several controlled release formulations of trifluralin in greenhouse and field. Weed Sci. 28:21-23.

19. Coffman, C.B., W.A. Genter, and B.S. Shasha. 1984. Herbicidal activity of controlled-release formulations of trifluralin. Indian J. Agric. Sci. 54:117-122.

20. Wienhold, B.J., A. Sadeghi, and T.J. Gish. 1993. Effect of starch encapsulation and temperature on volatilization of atrazine and alachlor. J. Environ. Qual. 22:162-166.

21. Blevins, R.L., G.W. Thomas, M.S. Smith, W.W. Frye, and P.L. Cornelius. 1983. Changes in soil properties after 10 years continuous non-tilled and conventionally tilled corn. Soil Tillage Res. 3:135-145.

22. Tyler, D.D., J.R. Overton, and A.Y. Chambers. 1983. Tillage effects on soil properties, disease, cyst nematodes, and soybean yields. J. Soil Water Conserv. 38:374-376.

23. Thomas, G.W., and W.W. Frye. 1984. Fertilization and liming. pp 87-126. In R.E. Phillips and S.H. Phillips (eds.) No-tillage agriculture. Van Nostrand Reinhold Co., New York.

24. Stearman, G.K., R.J. Lewis, L.J. Tortorelli, and D. D. Taylor. 1989. Herbicide reactivity of soil organic matter in no-tilled and tilled cotton. Soil Sci. Soc. Am. J. 53:1690-1694.

25. Christensen, L.A., and P.E. Norris. 1993. A comparison of tillage systems for reducing soil erosion and water pollution. Agric. Econ. Rep. No. U.S. Dept. Agric., Washington, DC. pp 27.

26. Wienhold, B.J., and T.J. Gish. 1994. Effect of formulation and tillage practice on volatilization of atrazine and alachlor. J. Environ. Qual. 23:292-298.

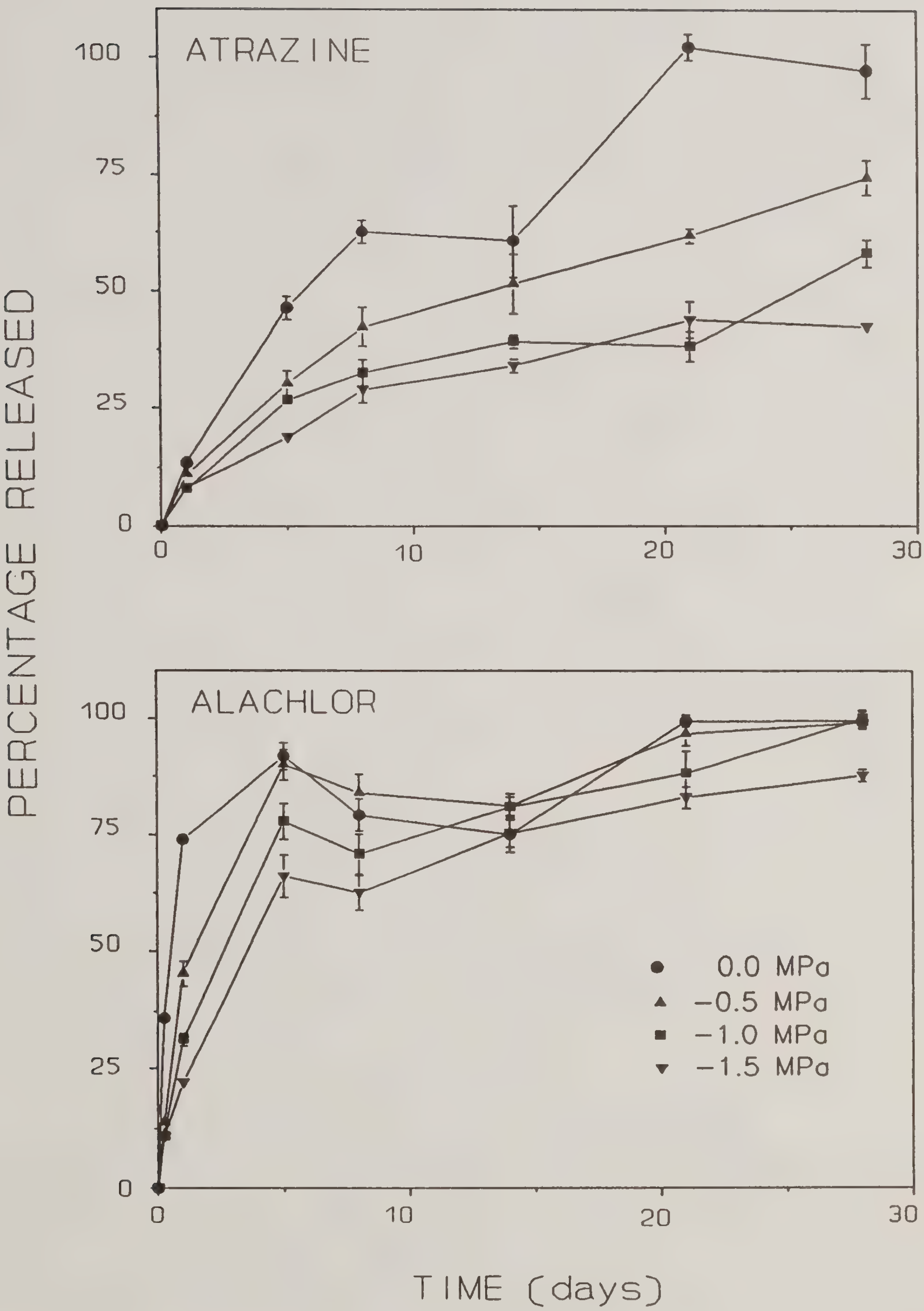

Figure 1. Effect of water potential imposed using polyethylene glycol on percentage release of atrazine and alachlor from starch granules as a function of time. Error bars indicate $\pm$ 1 standard error of the mean.

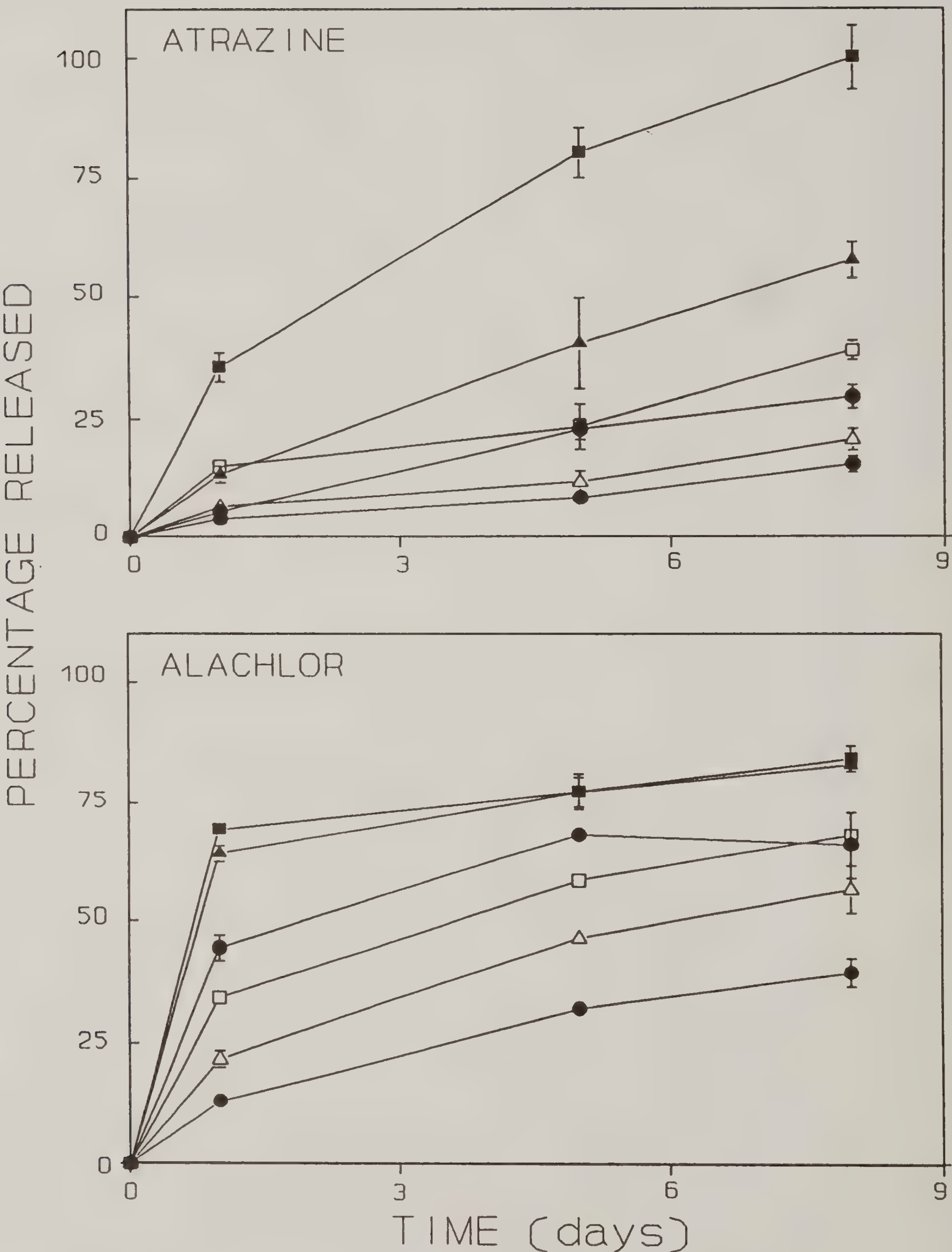

Figure 2. Percentage release of atrazine and alachlor from starch granules as a function of time, temperature [15 (●), 25 (▲), and 35° (■)] and water potential [0.0 MPa (filled symbols) and -1.0 MPa (open symbols)].

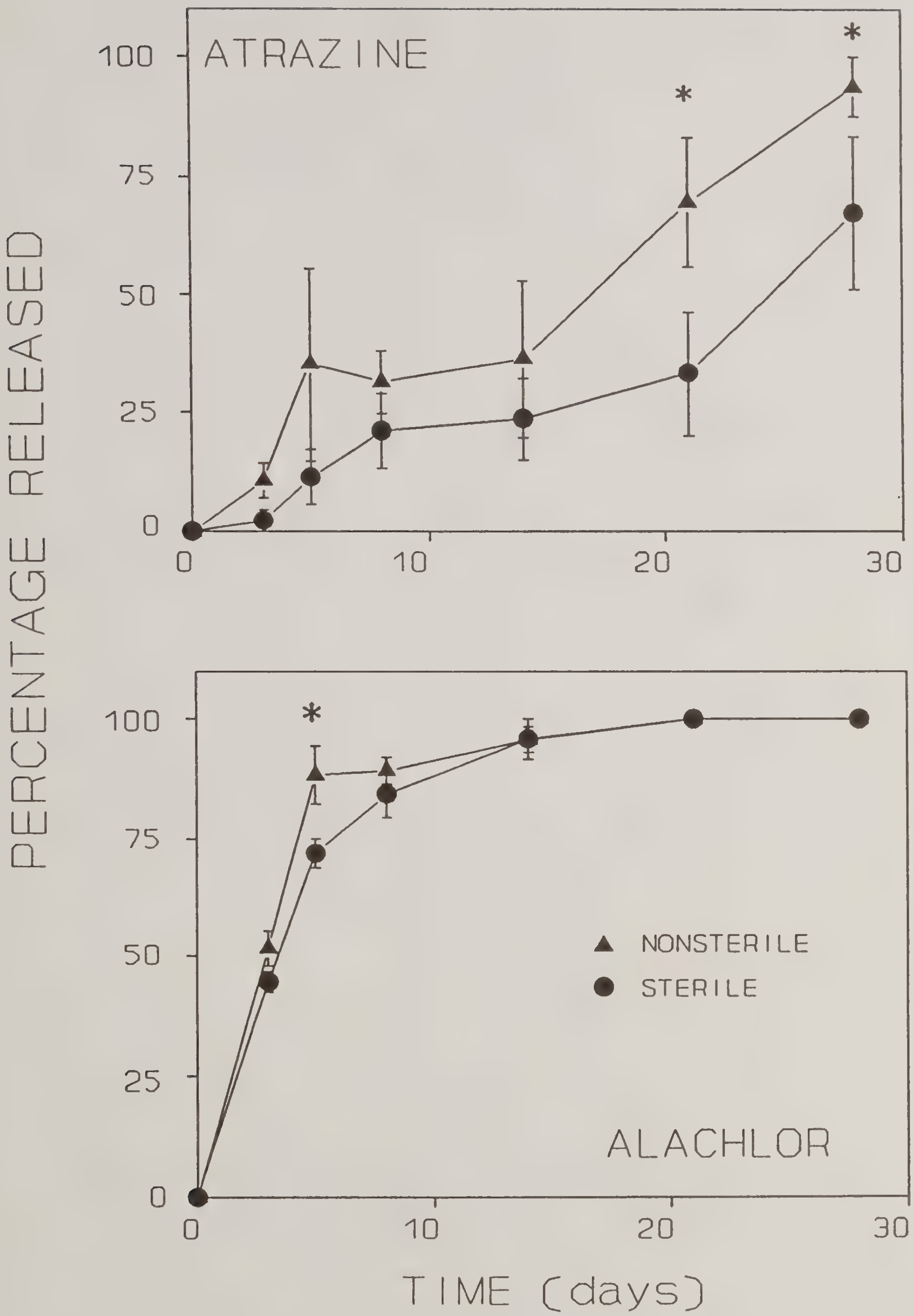

Figure 3. Effect of soil microbes on percentage of atrazine and alachlor released from starch granules as a function of time. Error bars indicate ± 1 standard error of the mean.

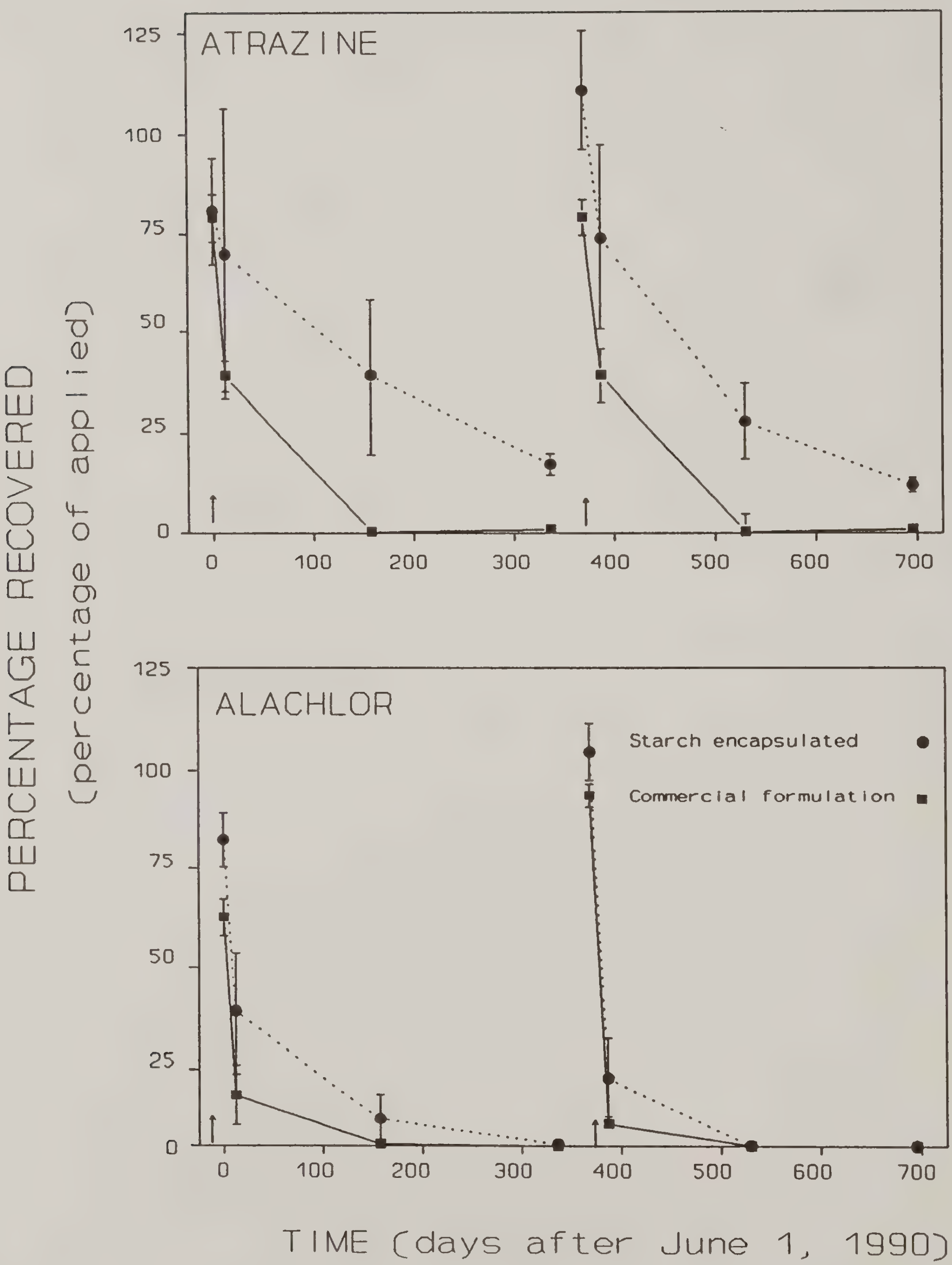

Figure 4. Field-scale recovery of herbicide as percentage of applied for atrazine and alachlor. Error bars indicate ± 1 standard error of the mean.

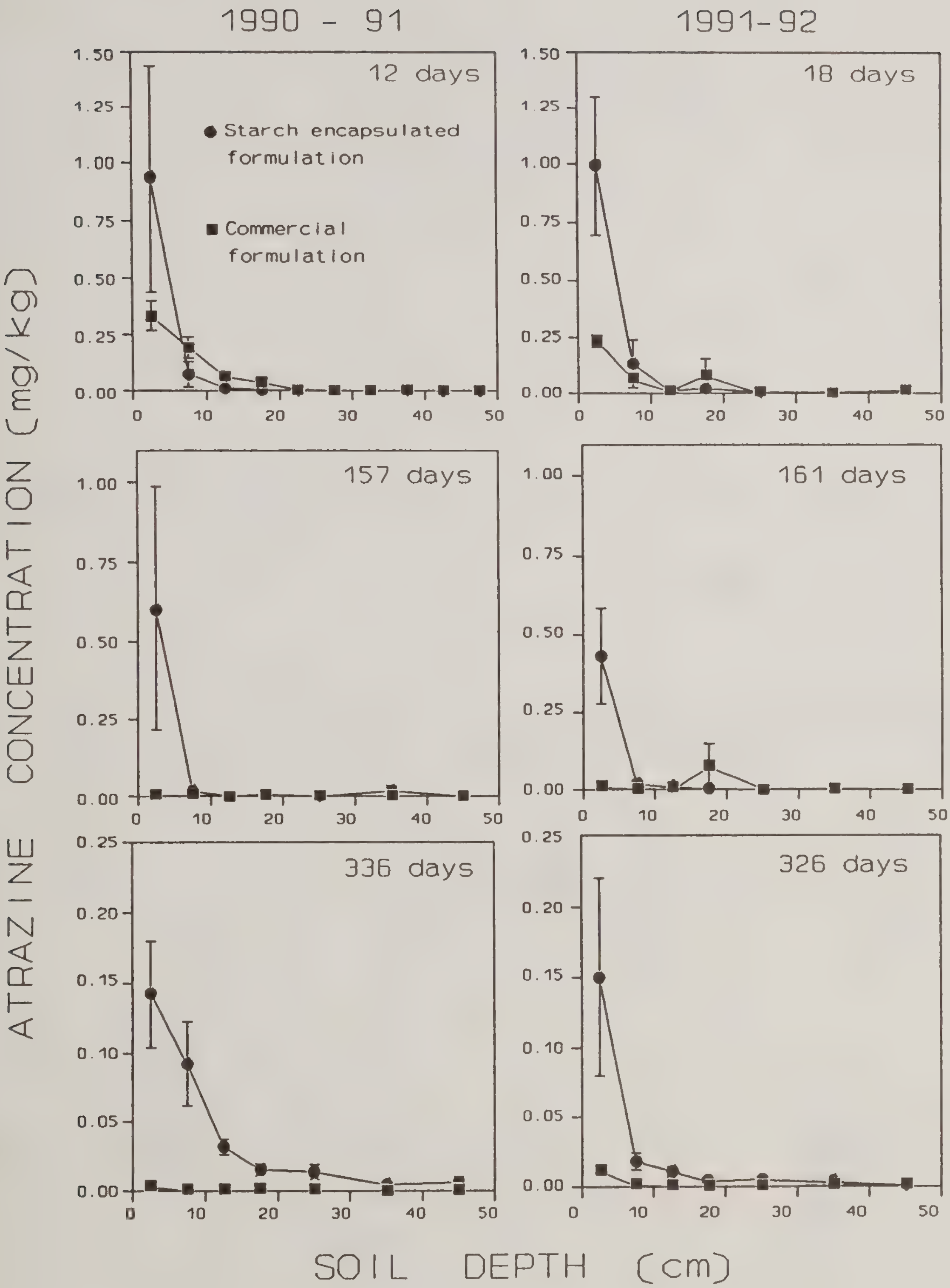

Figure 5. Comparison of field-scale atrazine soil concentrations as either SE or CF. Error bars indicate ± 1 standard error of the mean.

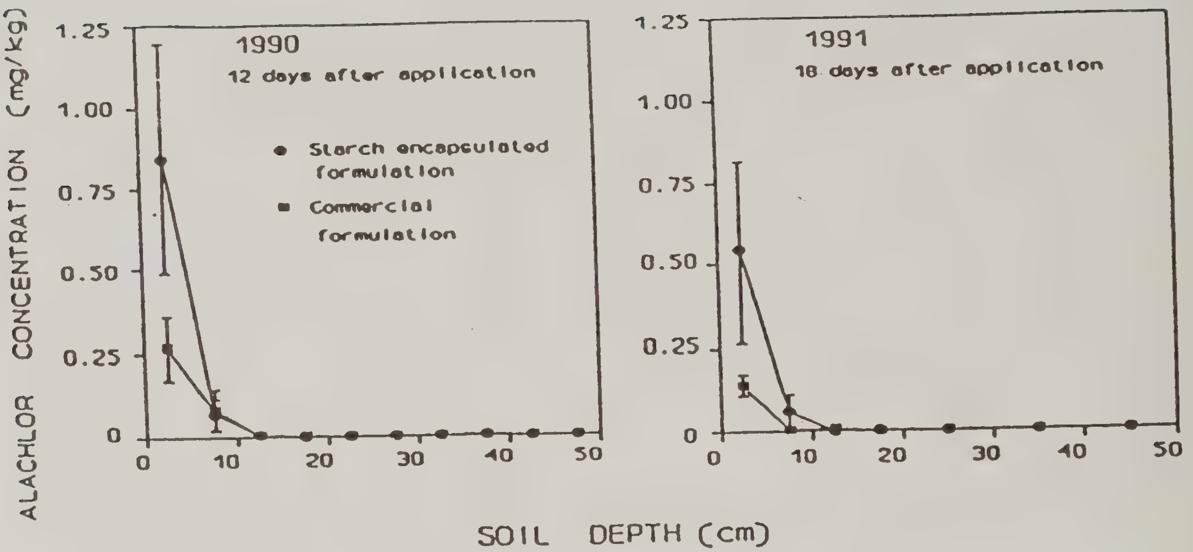

Figure 6. Comparison of alachlor soil concentrations as either SE or CF. No quantifiable amounts of alachlor detected in the last two sampling periods of 1991 and 1992. Error bars indicate $\pm$ 1 standard error of the mean.

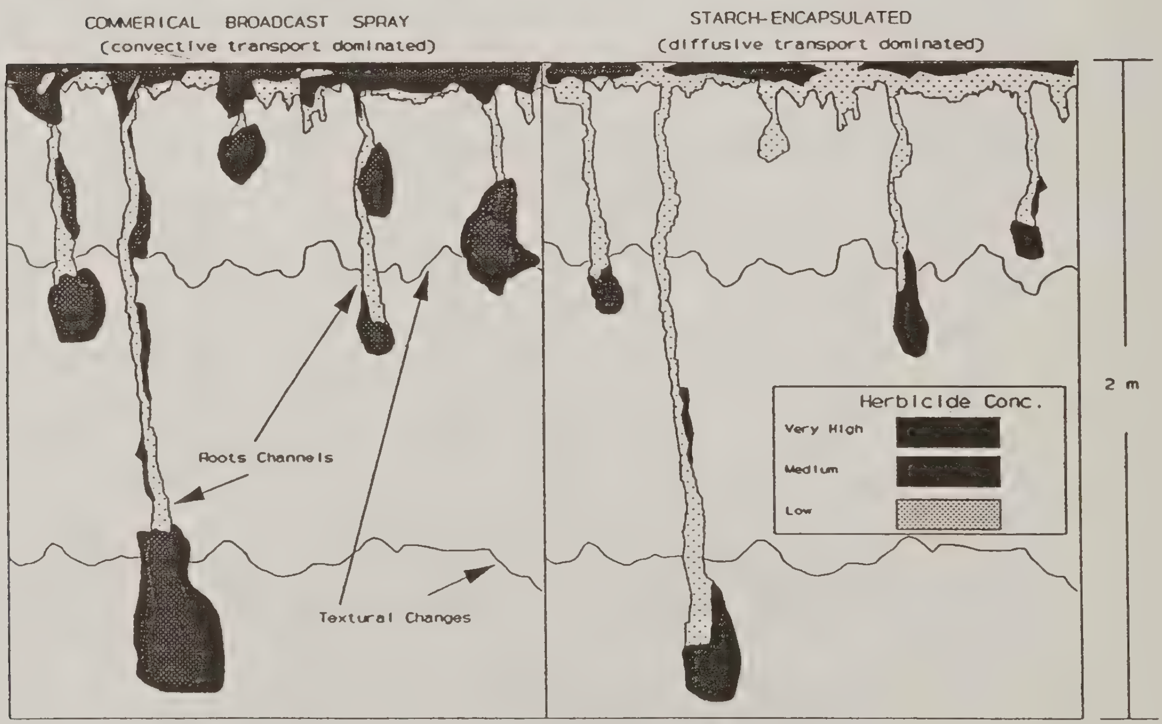

Figure 7. Hypothetical comparisons of SE and CF mobility in soil.

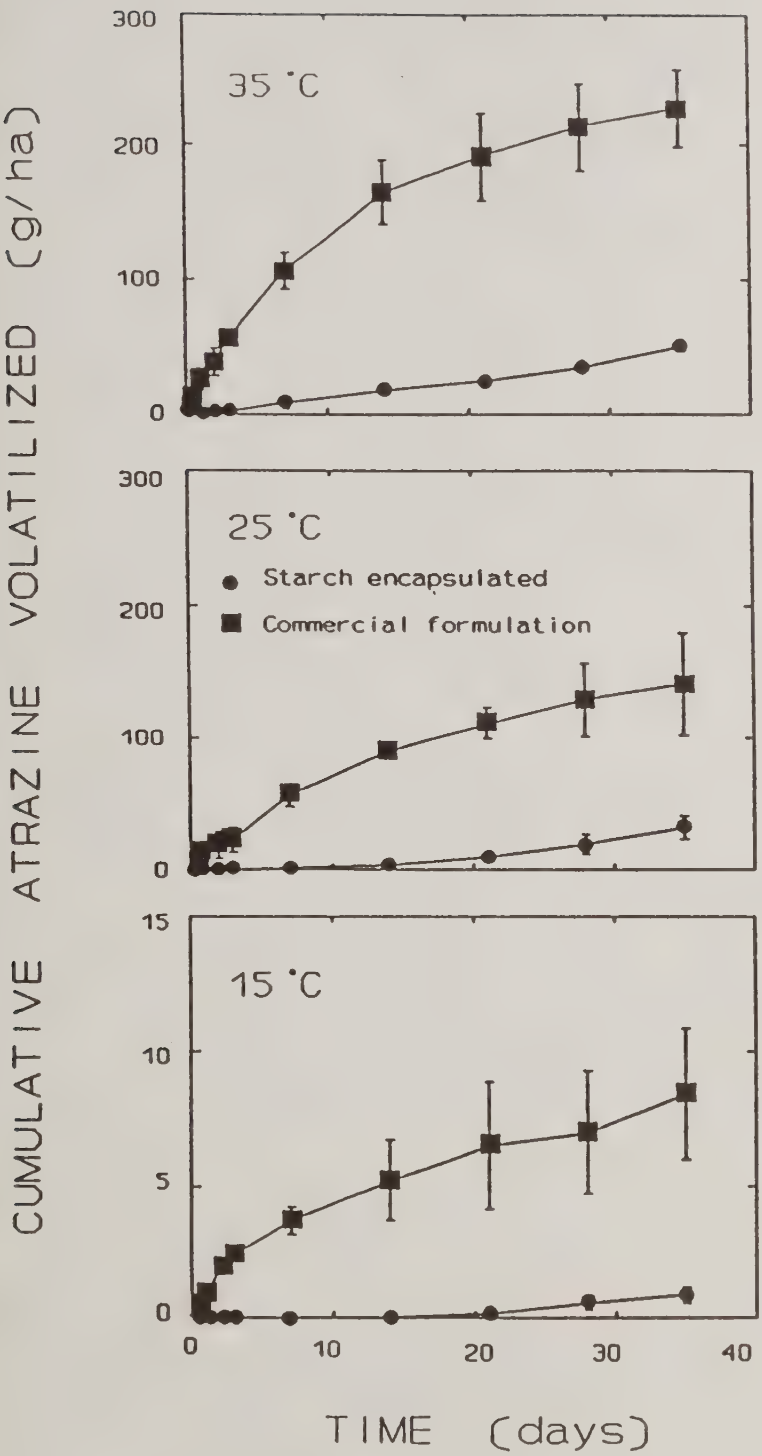

Figure 8. Cumulative atrazine volatilized as a function of temperature (15, 25, and 35°C) for SE and CF. Error bars denote the range of values observed. Note difference in Y-axis scale among graphs.

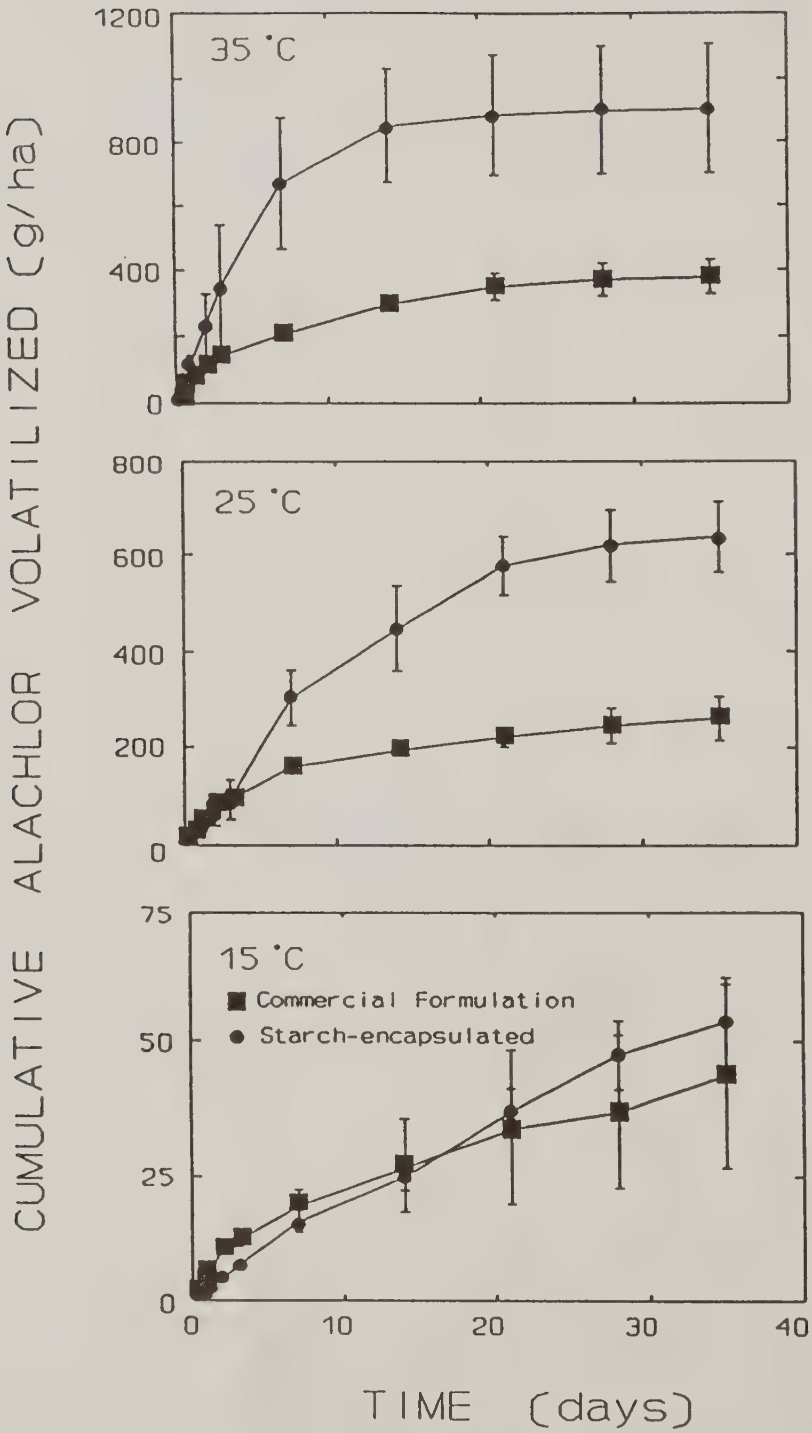

Figure 9. Cumulative alachlor volatilized as a function of temperature (15, 25, and 35°) for SE and CF. Error bars denote the range of values observed. Note difference in Y-axis scale among graphs.

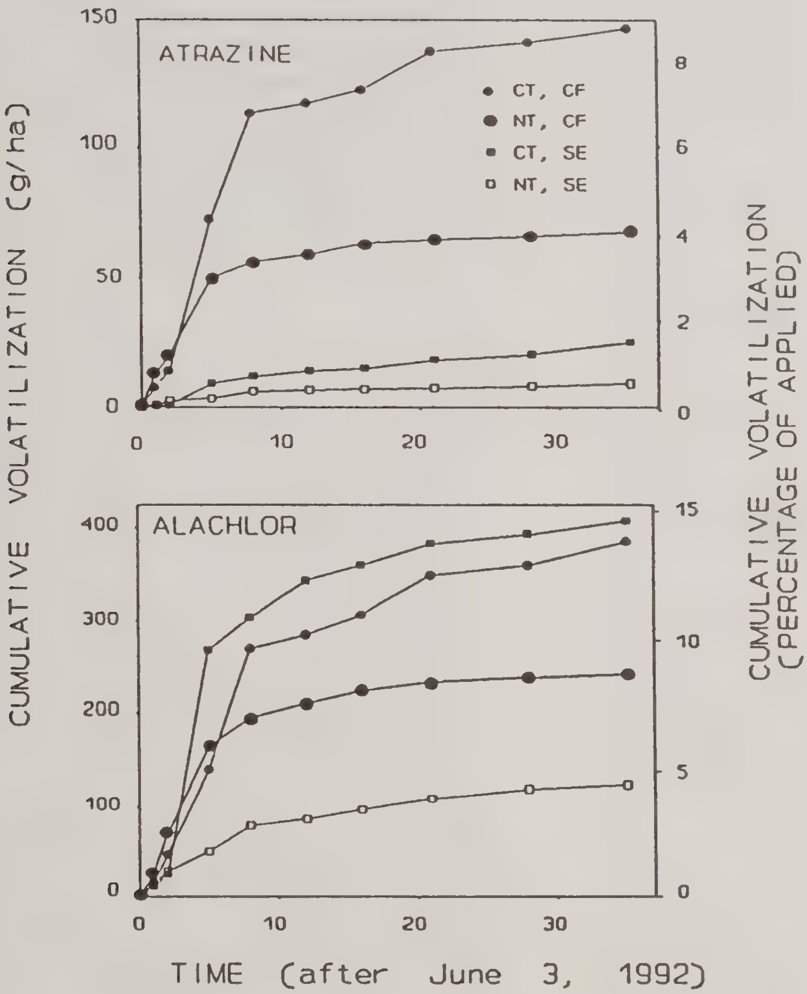

Figure 10. Cumulative volatilization of starch encapsulated and commercial atrazine and alachlor under conventional and no-tillage practices.

Mobility, Transport And Environmental Impact Of Starch Encapsulated Formulations Of Herbicides

Michael V. Hickman and Marvin M. Schreiber

The development and use of controlled release formulation of agrichemical products could alleviate many of the current environmental concerns. Experimental starch-encapsulated (SE) formulations of herbicides have demonstrated their capability to reduce agrichemical losses due to volatility, movement in surface runoff water, and leaching through the soil profile including movement via macropore flow. Trials using packed soil columns and intact soil blocks have demonstrated the effectiveness of SE atrazine formulations to reduce leaching. These trials routinely show reductions in atrazine leaching of 65% to 85% of the leaching of commercially formulated (CF) atrazine. Field trials which monitor atrazine in soil cores over the course of the season have confirmed these findings at several locations. Atrazine concentrations in surface runoff from SE treated plots were reduced 80% compared with the CF atrazine in field trials under high rainfall. In season long field trials the SE treatments reduced atrazine losses measured at the field edge by 40%. Extended residual activity in rotational crops from SE have been shown to not be problematic in labeled crop rotations thus far tested. Considering that all of the SE formulations tested are experimental, the results suggest that when the formulations are optimized for each active ingredient or cropping situation, the use of SE formulations could have a significant impact on the environmental contamination of soils and water from non-point agricultural sources.

Introduction

Environmental concerns have come to the forefront in agriculture in the United States and Worldwide. These include potential contamination of groundwater (1-2) and surface water (3-4) resources.

Modern agricultural production systems depend upon inputs of pesticides in order to meet the high demands for food and fiber. Herbicides are a significant portion of the total pesticides used. For example, the corn (*Zea mays* L.) and soybean (*Glycine max* L.) production region of the midwestern United States utilizes over 36,000 t of two herbicides, atrazine [6-chloro-*N*-ethyl-*N*'-(1-methylethyl)-1,3,5-triazine-2,4-diamine] and alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxy-methyl)acetamide] (5).

Atrazine has been frequently detected in groundwater (5) and surface water (6) and has been reported in rainfall (4). Chemically, atrazine is a relatively stable molecule with a water solubility of 33 mg/L at 27°C, vapor pressure of 3.9 μPa at 25°C and an average persistence at recommended use rates of < 1 year (7). Atrazine herbicide has been shown to leach through soil and move with surface water under normal usage (8). Schreiber et al. (9) suggested that starch encapsulated (SE) formulations of pesticides could reduce leaching losses while maintaining required efficacy.

Development of starch encapsulation technology has progressed from a batch chemical process to a continuous, mechanical extrusion process since it's beginnings in the mid 1970's (10-15). Encapsulation in starch involves the entrapment of pesticides within a solid starch matrix. The resulting granules exhibit controlled release properties and have the potential to control pesticide movement from site of application through leaching, water runoff, or volatility (8-9, 12, 16-17). Current data suggest that experimental SE formulations significantly modify the mobility of atrazine in soil, in comparison with commercial formulations (CF) (18-20).

This paper presents data from recent research to support the assertion that experimental SE formulations can reduce herbicide leaching through soil and movement with surface water flow. Additionally, data will be presented to address concerns of increased residual activity from use of SE formulations.

Leaching

Schreiber et al. (9) suggested SE formulations as an approach to controlling the leaching of agricultural chemical. Many SE formulations have been produced and tested in systems ranging from packed soil columns to field scale trials.

Several experimental SE formulations of atrazine were tested using packed soil columns at West Lafayette, IN, to determine the initial mobility of atrazine on different soil types. The SE formulations were produced by mechanical extrusion (15) using pearl cornstarch and

---

Hickman is a Research Agronomist, Schreiber is a retired Research Leader, Insect and Weed Control Research Unit, USDA-ARS-MWA, Purdue University, W. Lafayette, IN 47907.

technical grade atrazine. The extruded material was collected, ground and screened to size (Table 1). Granules were sized into three categories with the larger granules able to pass a 1.4 mm screen but retained on a 0.85 mm screen, the midsize granules able to pass a 0.85 mm screen but retained on a 0.425 mm screen, and the fine granules passing a 0.425 mm screen. SE formulations prepared in this manner may have from 10 to 15% of the active ingredient (a.i.) present at or near the surface resulting in a slightly faster initial release rate with some compounds. This material can be removed by briefly washing the granules in an organic solvent. This was done in order to produce two of the formulations described in Table 1 (443C and 443D). This was done in order to examine the effect of the early release on the leaching of atrazine.

Packed Soil Columns

Two soils, a Miami silt loam (fine-loamy, mixed, mesic Typic Hapludalfs, pH = 6.5, and 3.8% organic matter) and a Tracy sandy loam (course loamy, mixed mesic Ultic Hapludalfs, pH = 6.4, OM = 2.6%) were collected, air-dried and screened through a 2 mm wire mesh. The < 2 mm fraction was used to pack aluminum leaching columns. The columns consisted of aluminum tubes 47.2 cm long and 7.6 cm in diameter with an open slot 1.9 cm wide and 38 cm long cut into the side. The slot was covered and sealed with an aluminum strip held in place by screw clamps. The bottom of the column was closed with a one-hole rubber stopper and the columns were uniformly packed to a soil bulk density of 1.5 g cm^{-3} with the air-dried soils. The packed columns were secured in a vertical position and saturated with 750 ml of distilled water added to the top of the column. The columns were allowed to drain for 24 h before an additional 380 ml of distilled water was added and the leachate collected to verify column uniformity of packing.

Atrazine was applied to the top of each tube at a rate equivalent to 3.36 kg of a.i. ha^{-1} and a 1 cm layer of washed silica sand was added to limit the disruption of the soil surface during addition of water. The herbicide treatments consisted of a commercial liquid formulation and SE formulations as described above and presented in Table 1.

The columns were leached with 250 ml of distilled water (equivalent to 5 cm rainfall). Leaching was accomplished at an approximate water flowrate of 4 ml min^{-1} and a 1 cm head of water was maintained on the column during the leaching. Columns were allowed to drain for 24 h and the leachate volume was recorded as an additional check of column uniformity. A second leaching event was performed in a like manner to the first using 150 ml of distilled water (3 cm rainfall). Following the drainage period for the second leaching the top of the columns were closed by insertion of a large rubber stopper and the columns were positioned horizontally in trays with the slotted side up. The slot covers were carefully removed and the columns were seeded with approximately 400 seeds of bentgrass (*Agrostis tenuis* Sibth.) as a bioassay species. The columns were maintained in the greenhouse for 14 days to allow for bentgrass growth and the extent of leaching was determined by measuring the distance from the top of the column to the point where bentgrass was unaffected. The trials were replicated three times, and the data were statistically analyzed by analysis of variance and means were separated by Fisher's protected least significant difference test (21).

SE formulations significantly reduced atrazine leaching on both soil types compared to the CF (Figure 1). Approximately 10 to 15% of the active ingredient is on or near the surface of SE formulations and can be removed by washing the SE with solvent. Washing the SE did not significantly change the atrazine leaching in this trial although the washed granules tended to leach less than the nonwashed granules. Granule size made no measurable difference in leaching on either soil type tested (Figure 1). When considered over both soil types, both granule sizes and washed vs. nonwashed the SE formulations reduced atrazine leaching by 75% compared to the CF.

Wauchope et al. (22) conducted similar trials on a Lakeland sand soil under unsaturated flow conditions. Treatments included SE atrazine, CF atrazine applied with and without a polymeric adjuvant designed as a 'leaching prevention' agent. The SE plus the polymeric agent reduced atrazine movement by 90% compared to the CF alone. Bioassay data from these trials showed that the atrazine had been retained in the upper portions of the column by the SE and SE plus polymeric adjuvant leading the authors to conclude that SE formulations may have a place in controlling atrazine movement.

Boydston (19) packed columns with screened Quincy loamy sand and treated the prewetted surface with a 90% CF of simazine (6-chloro-*N*,*N'*-diethyl-1,3,5-triazine-2,4-diamine), a herbicide similar to atrazine, and a SE formulation of simazine in pearl cornstarch.

The treatments were allowed to equilibrate for 24 h before leaching. The SE formulations reduced simazine movement by over 80% compared to the CF. The author concluded that SE formulations could significantly reduce the early season leaching potential of simazine. The data lead the author to express concern that SE formulations may result in unacceptable levels of residual simazine available for early season leaching in the following year.

Fleming et al. (23) used packed soil columns and bioassays to determine the effect of granule size, clay amendments and processing parameters on the leaching potential and efficacy of SE atrazine formulations. The trials used 7.5 cm diameter by 40 cm columns packed with Plainfield sand (Typic Udipsamment, mixed mesic) soil that was 98% sand, 0.7% organic matter and had a pH = 6.2. Treatments included a 90% dry flowable CF and SE formulations in pearl cornstarch with 11% atrazine. The columns were prewetted, treated with herbicides and then subjected to leaching with a total of 15.2 cm of water applied at a rate of 1.3 cm in 20 min per day for 12 days. Leachate was collected and atrazine content determined. When leaching was complete, the soil columns were sectioned into 5 cm segments and atrazine content was determined. The authors recovered 68% more atrazine from the top 5 cm of the SE treated columns than from the CF treatments. The CF resulted in a pulse of atrazine that moved through the column and the peak concentration was at the 25-30 cm depth. A related efficacy trial also reported found that differences in bioavailability between CF and SE formulations could be overcome by decreasing the granule size.

Intact Soil Columns

A leaching study using intact soil blocks was carried out at West Lafayette, IN, in the fall of 1990. Columns were removed from continuous soybean plots, one with no-till and one with a fall chisel plow tillage system. The chisel plow system included secondary tillage in the spring for seedbed preparation and one cultivation in early season. The columns were removed in the fall after soybean harvest but before fall tillage. The soil at this site was a Treaty silt loam with pH of 6.3 and 21, 50, and 29%, sand, silt and clay, respectively. The columns were 76 cm by 76 cm by 30 cm and were taken from an interrow space that normally did not receive tractor traffic. The columns were encased in cement in the field and supported with wire mesh beneath to prevent collapse during transport to a rain simulation facility. Herbicide treatments of atrazine at 3.36 kg/ha^{-1} as liquid CF or as SE formulation 149B (Table 1) were added 1 h before rainfall began. The columns were situated to allow for the collection of all effluent water and to not allow any water to run off the column surface. Rainfall was applied in two events using distilled water. The first rainfall was applied at a rate of 40 mm h^{-1} for 2 h followed by a 1 h rest and a second rain of 25 mm h^{-1} for 2 h. Effluent water from the columns was collected for the first hour and then in 15 min increments until the end of the rainfall (300 min). The columns were allowed to drain overnight and this drainage was also collected and analyzed. Atrazine content in the effluent waters was determined by solid phase extraction and gas chromatography. The treatments were replicated three times.

The effluent volume from no-till and chisel plow tillage blocks was nearly equal in this trial (Figure 2). The lack of differential may be due to the long time that passed after the secondary tillage in the chisel plow tillage allowing the system to reform macropores that may have been disrupted by tillage. The SE formulation reduced the total atrazine leaching by 80 and 60% over the CF, for chisel and no-till, respectively (Figure 3A and 3B). The SE formulations also eliminated the atrazine surge that is often present with early water flow on CF treatments. This is consistent with packed column data reported by Fleming et al. (23).

Gish et al. (18) measured atrazine movement in small, undisturbed soil columns taken from an established no-till management site. The columns (45 cm^2 by 3 cm) were treated with either technical grade atrazine or SE atrazine at the same rate. The columns were leached with a total of 16.1 pore volumes of water applied through a drip irrigation system. The water applications were designed to favor preferential flow and all effluent waters were analyzed for atrazine. After 16.1 pore volumes of water 35% of the technical atrazine had moved through the columns compared with only 3% of the SE atrazine formulation.

Field Studies

The ability of SE formulations to reduce leaching in packed and intact soil columns translates to the field. Trials using CF and SE formulations of atrazine were conducted on a Treaty silt loam soil at West Lafayette, IN, in 1990 and 1991. Atrazine was applied at rates of 2.24 kg ha^{-1} in 1990 and 2.8 kg ha^{-1} in 1991 in a study that used 3 by 15 m plots in a randomized complete block design with four replications. Soil cores were

taken from two locations within each plot, to a depth of 120 cm, 28 weeks after treatment in 1990 and 20 weeks after treatment in 1991. The cores were divided into 15 cm sections except for the upper 15 cm which was sectioned into 7.5 cm sections. All of the core sections were extracted and the atrazine concentration was determined.

The total quantity of atrazine recovered from the entire 120 cm core was not different for the two formulations in 1990, however, atrazine recovery from the entire core was three times greater for the SE that the CF in 1991. Below normal precipitation throughout the 1991 growing season may help explain the increased recovery of the SE formulations. From a leaching perspective, the total recovery is not as important as the distribution of the herbicide in the soil profile. In 1990 over 95% of the atrazine recovered from the SE treatments was present in the upper 15 cm of soil (Table 2) compared with only 63% of the CF. Both formulations had over 90% of the recovered from the top 15 cm in 1991, a below normal precipitation year.

Surface Movement

An experimental site was established in June of 1992 to determine the effects of residue cover, tillage practice (24) and herbicide formulation on soil erosion and herbicide loss via surface water runoff. The study was located near Lexington, IL, on two field sites with long term cropping histories. Site 1 was a conventionally tilled field managed in a corn-soybean rotation. The previous crop was corn. The soil was a Saybrook silt loam (fine-silty, mixed, mesic Typic Agriudoll). The trial was designed to utilize a rain simulator to apply controlled rainfall to 1 by 2 m, interill plots. Atrazine was applied as a spray for the CF liquid and as 149B SE granules (Table 1) at 2.8 kg ha^{-1} approximately 1 h before rainfall began. Treatments at site 1 were: freshly tilled + CF, freshly tilled + SE, freshly tilled + SE + residue removed, and freshly tilled + CF + residue removed. The treatments were replicated 4 times. Site 2 was located on a long term (15 + years) no-till field in a corn soybean rotation with corn as the previous crop. Treatments were: no-till + Cf, no-till + SE, no-till + CF + residue removed and no-till + SE + residue.

Rainfall was applied to each plot at an intensity of 70 mm h^{-1} for 90 min using a programmable rainfall simulator. The rainfall simulator using distilled water, was positioned 3 m above the plot surface. Runoff samples were collected at 5 min intervals during the rainfall and runoff and infiltration rates were calculated. Samples for herbicide analysis were spiked with an internal standard and stored under refrigeration until processed. The water samples were filtered, sediment content determined and the atrazine extracted using solid phase extraction techniques. Herbicide residues were quantified by gas chromatography.

Residue cover was estimated visually and quantified by removal and weighing from the residue removal plots. The conventional tillage plots had approximately 30% cover by visual estimate (0.26 kg m^{-2}) while the no-till plots had 100% residue cover (1.12 kg m^{-2}). The infiltration rate was essentially 100% on the no-till plots with the residue in place so no herbicide loss via surface movement occurred. All comparisons of formulation were made using the plots with residue removed. Runoff with residue removed occurred sooner from the no-till plots than from the conventionally tilled plots, however, the final runoff and infiltration values were nearly identical (23 vs. 25 mm h^{-1} for no-till and conventional, respectively). Equivalent runoff did not mean equivalent sediment losses. No-till soils were structurally stronger than the conventionally tilled soils resulting in nearly a 3-fold increase in sediment loss from the conventional tillage treatments. Further, the surface flow in conventional tilled plots was more concentrated and channeling added to the sediment losses.

When data were averaged over tillages, the CF lost 1.65% of applied atrazine in the runoff water compared with 0.35% loss for the SE formulations. This is a reduction of nearly 80% by the SE. A statistically significant interaction occurred between formulation and tillage in this trial (Figure 4). Runoff losses from CF atrazine on conventional tillage were slightly less than losses from the SE. On the no-till plots the atrazine lost in runoff water was more than 20-fold greater than from the SE formulations.

Mills et al. (20) conducted a study on corn plots near Topeka, KS, equipped to allow for collection of all surface runoff water. Herbicides were applied at 2 kg ha^{-1} and incorporated into the top 5 cm of soil with a rotory tiller. Natural rainfall and sprinkler irrigation were used to add a total of approximately 42 cm of water to the plots over the season.

SE formulations reduced the initial flush of atrazine leaving the field in runoff immediately after application by a factor of 20 compared to the CF. The authors concluded that the use of SE atrazine could reduce the mass of atrazine entering surface waters by 40%.

Additionally, SE formulations would produce a more even flux of herbicides through time resulting in improved surface water quality.

Residual Activity

Laboratory and field studies have demonstrated the abilities of SE formulations to slow herbicide availability, reduce herbicide leaching losses and reduce the movement of herbicides in surface water. It follows then, that SE formulations have an increased potential for residual activity in rotational crops. Atrazine has a residual life at recommended use rates of approximately 1 year (7). Some crops, including oats (*Avena sativa* L.) and other small grains are restricted from rotations which include atrazine because of this long residual activity.

Vail et al. (25) conducted studies designed to measure the dissipation of atrazine under field conditions at West Lafayette, IN, beginning in the spring of 1991. Treatments included CF atrazine and SE atrazine formulations 149A, 149B, and 149C (Table 1) applied preemergence to corn at rates of 1.12, 2.24, and 3.36 kg ha^{-1} on June 10, 1991. Soil samples were taken before treatment and periodically throughout the season and the following spring. The soil cores were divided into segments corresponding to depths of 0 to 7.5, 7.5 to 15, 15 to 30, and 30 to 45 cm and were analyzed for atrazine by methanol extraction and gas chromatography.

Oats were planted on the site on April 7, 1992, as a bioassay crop. The injury on oats was evaluated on May 25, 1992, and the oat crop was killed by treatment with a postemergence herbicide. Soybeans were no-till planted into the spray killed oats on May 27, 1992, and were grown to maturity. Soybeans are a common rotational crop in the corn producing areas of the midwestern United States and are sensitive to atrazine residual activity.

Late corn planting and treatment in 1991, in combination with an unusually dry growing season resulted in poor weed control from all treatments as well as reduced crop growth. The five months following planting had only 50% of normal rainfall. Detectable levels of atrazine were present in soil samples from all three treatment rates and all formulations (Figure 5). The majority of the atrazine detected was in the upper 7.5 cm of the soil profile and the SE formulations 149A and 149B had significantly greater levels of residual atrazine than the smaller 149C and the CF. No differences in residual levels were detected at depths below 7.5 cm except for the CF at the 30 to 45 cm level in the 2.24 kg ha^{-1} rate. The pattern of greater residues in the upper portions of the profile is expected given the demonstrated ability of SE formulations to reduce leaching. Further, the effect of increasing granule size of atrazine release in SE formulations can be seen in these data. The larger granules tend to have the highest residuals.

The injury to the oat bioassay crop (Figure 6) confirmed the soil residual levels. All of the formulations resulted in carryover atrazine that injured the oats. The SE formulations had significantly more oat injury than the CF at the higher rates. At the 1.12 kg ha^{-1} rate the larger granule SE caused more injury that the smallest sized SE or the CF. The substantial oat injury seen in this trial was not repeated in subsequent trials with more normal precipitation patterns. Oats are very sensitive to atrazine and residues that injure oats may be well below the level that would be problematic for labeled rotational crops. This is demonstrated by the soybean crop grown following the oats in this trial. No visible injury could be detected in the soybean crop and the yields (Table 3) were not statistically different for any of the treatments.

Summary

All of the trials discussed in this paper and all of those in the literature were performed using experimental SE formulations. These formulations were not optimized or altered to improve their efficacy or their ability to control release or other factors. It is logical to assume that with a focused effort aimed at improving the SE formulation for a particular herbicide or cropping system the advantages demonstrated with the experimental formulations could be even greater. The SE formulations controlled leaching in several different soils and under many conditions. They reduced the amount of atrazine moving off site in surface water in short term, high rainfall situations as well as over the entire growing season. While SE formulations may result in elevated residue in the upper soil profile it does not appear to present an insurmountable problem. Something as simple as reducing the granule size resulted in substantially reduced residues. Normal rotational crops were not adversely affected by the residues of high rates even following a dry growing season that would accentuate the residue problem.

References

1. Romander, L. 1988. Groundwater logic, Agrichemical Age 32:26-27.

2. Lenard, R.L., and W.G. Kinsel. 1988. Evaluating groundwater contamination potential from herbicide use. Weed Technology 2:207-216.

3. Weed Science Society of America. 1991. Position statement on water quality. Weed Technology 5:921.

4. Busher, H.R. 1990. Atrazine and other S-triazine herbicides in lakes and in rain in Switzerland. Environmental Science Technology 24:1049-1058.

5. EPA. 1992. Another Look: National survey of pesticides in drinking water wells. Phase II report. EPA 579/09-91-020. U.S. Environmental Protection Agency, Washington, DC.

6. Goolsby, D.A., E.M. Thurman, and D.W. Kolpin. 1990. Geographic and temporal distribution of herbicides in the uppermidwestern United States, 1989-1990. U.S. Geological Survey Water-Resources Investigations Report 91-4034, p. 183-188.

7. Herbicide Handbook. 1989. Sixth edition, Weed Science Society of America, Champaign, IL.

8. Wienhold, B.J., and T. J. Gish. 1993. Effects of formulation and tillage practice on volatilization of atrazine and alachlor. Journal Environmental Quality. In Press.

9. Schreiber, M.M., B.S. Shasha, D. Trimnell, and M.D. White. 1987. Controlled release herbicides. *In* C. C. McWhorter and M. Debhardt. eds. Methods of Applying Herbicides. pp. 177-191. Monogram No. 4. Weed Science Society of America, Champaign, IL.

10. Shasha, B.S., W.M. Doane, and C.R. Russell. 1976. Starch-encapsulated pesticides for slow release. Journal Polymer Science Polymer Letters Edition 14:417-420.

11. Shasha, B.S., D. Trimnell, and F. H. Otey. 1981. Encapsulation of pesticides in a starch-calcium adduct. Journal Polymer Science, Polymer Chemical Edition 19:1891-1899.

12. Trimnell, D., B.S. Shasha, R.E. Wing, and F.H. Otey. 1982. Pesticide encapsulation using a starch-borate complex as wall material. Journal Applied Polymer Science 27:3919-3928.

13. Wing, R.E., S. Maiti, and W.M. Doane. 1987. Factors affecting release of butylate from calcium in ion-modified starch-borate matrices. Journal Controlled Release 5:79-85.

14. Wing, R.E., S. Maiti, and W.M. Doane. 1987. Effectiveness of jet-cooked pearl starch as a controlled release matrix. Starch/Starke 39:422-425.

15. Carr, M.E., R.E. Wing, and W.M. Doane. 1991. Encapsulation of atrazine within a starch matrix by extrusion processing. Cereal Chemistry 68: 262-266.

16. Schreiber, M.M., M.V. Hickman, and G.D. Vail. 1993. Starch-encapsulated atrazine: Efficacy and transport. Journal Environmental Quality. 22:443-453.

17. Schreiber, M.M., and M.D. White. 1980. Granule structure and rate of release with starch-encapsulated thiocarbamates. Weed Science 28: 685-690.

18. Gish, T.J., M.J. Schoppet, C.S. Helling, A. Shirmohammadi, M.M. Schreiber, and R.E. Wing. 1991. Transport comparison of technical grade and starch encapsulated atrazine. Transactions of American Society of Agricultural Engineers. 34:1738-1744.

19. Boydston, R.A. 1992. Controlled release starch granular formulations reduce herbicide leaching in soil columns. Weed Technology 6:317-321.

20. Mills, M.S., E.M. Thurman, R.E. Wing, and P.L. Barnes. 1990. Dissipation of starch-encapsulated herbicides: A field comparison with powdered herbicides. U.S. Geological Survey, Water Resources Investigation 91-4034 p. 203-209.

21. Steele, R.G.D., and J.H. Torrie. 1980. Principles and procedures of statistics: A biometrical approach. 2nd Edition. McGraw-Hill Book Company, New York.

22. Wauchope, R.D., N.C. Glaze, and C.C. Dowler. 1990. Mobility and efficacy of controlled-release

formulations of atrazine. Weed Science Society of America Abstract 30:72.

23. Fleming, G.L., L.M. Wax, and F.W. Simmons. 1992. Leachability and efficacy of starch-encapsulated atrazine. Weed Technology 6:297-302.

24. Bradford, J.M., and C. Huang. 1993. Interrill soil erosion as affected by tillage and residue cover. Soil Tillage Research. In Press.

25. Vail, G.D., M. M. Schreiber, and M.V. Hickman. 1992. Atrazine residues from commercial and starch encapsulated formulations. Proceedings North Central Weed Science Society 47:19, Chicago, IL.

Table 1. Characteristics of atrazine formulations used in trials at West Lafayette, IN

Formulation	Granule Size passed-retained		Active Ingredient (a.i.) Loading
	mm		%
149A	1.4	0.85	11.1
149B	0.85	0.425	11.1
149C	0.425		11.1
443A	1.4	0.85	10.0
443B	0.85	0.425	10.0
443C	1.4	0.85	9.0 [a]
443D	0.85	0.425	8.6 [a]
4L	commercial liquid		43.0

[a]Formulations 443C and 443D were surface washed with solvent to remove nonencapsulated herbicide following grinding and screening.

Table 2. Distribution of atrazine residues in soil columns taken from field trials at West Lafayette, IN 1990 and 1991

Treatment	Formulation	Rate	Depth (cm) 0-7.5	7.5-15	15-30	30-45	45-60	60-75	75-90	90-105	105-120
			Atrazine recovered								
1990-28 weeks after application											
		kg ha^{-1}	%								
Atrazine	4L	2.24	39.2	23.4	16.1	3.8	0.6	4.8	5.0	6.1	1.0
Atrazine	SE, 14-20	2.24	73.4	21.9	4.0	0.0	0.0	0.0	0.0	0.0	0.71
1991-20 weeks after application											
Atrazine	4L	2.8	82.2	10.5	2.9	0.0	0.8	1.9	1.7	0.0	0.0
Atrazine	SE, 14-20	2.8	90.2	7.2	1.1	0.0	0.1	0.3	0.6	0.5	0.0

Table 3. 1992 Soybean yields in atrazine residue trials at West Lafayette, IN. Atrazine treatments applied June 10, 1991

Treatment	Formulation	Rate	Yield
		kg ha^{-1}	
Atrazine	149A	3.36	3017
Atrazine	149B	3.36	3106
Atrazine	149C	3.36	3329
Atrazine	4L	3.36	3214
Atrazine	149A	2.24	3314
Atrazine	149B	2.24	3270
Atrazine	149C	2.24	3436
Atrazine	4L	2.24	3210
Atrazine	149A	1.12	3191
Atrazine	149B	1.12	3234
Atrazine	149C	1.12	3137
Atrazine	4L	1.12	3207
Untreated	-----	0.0	3138

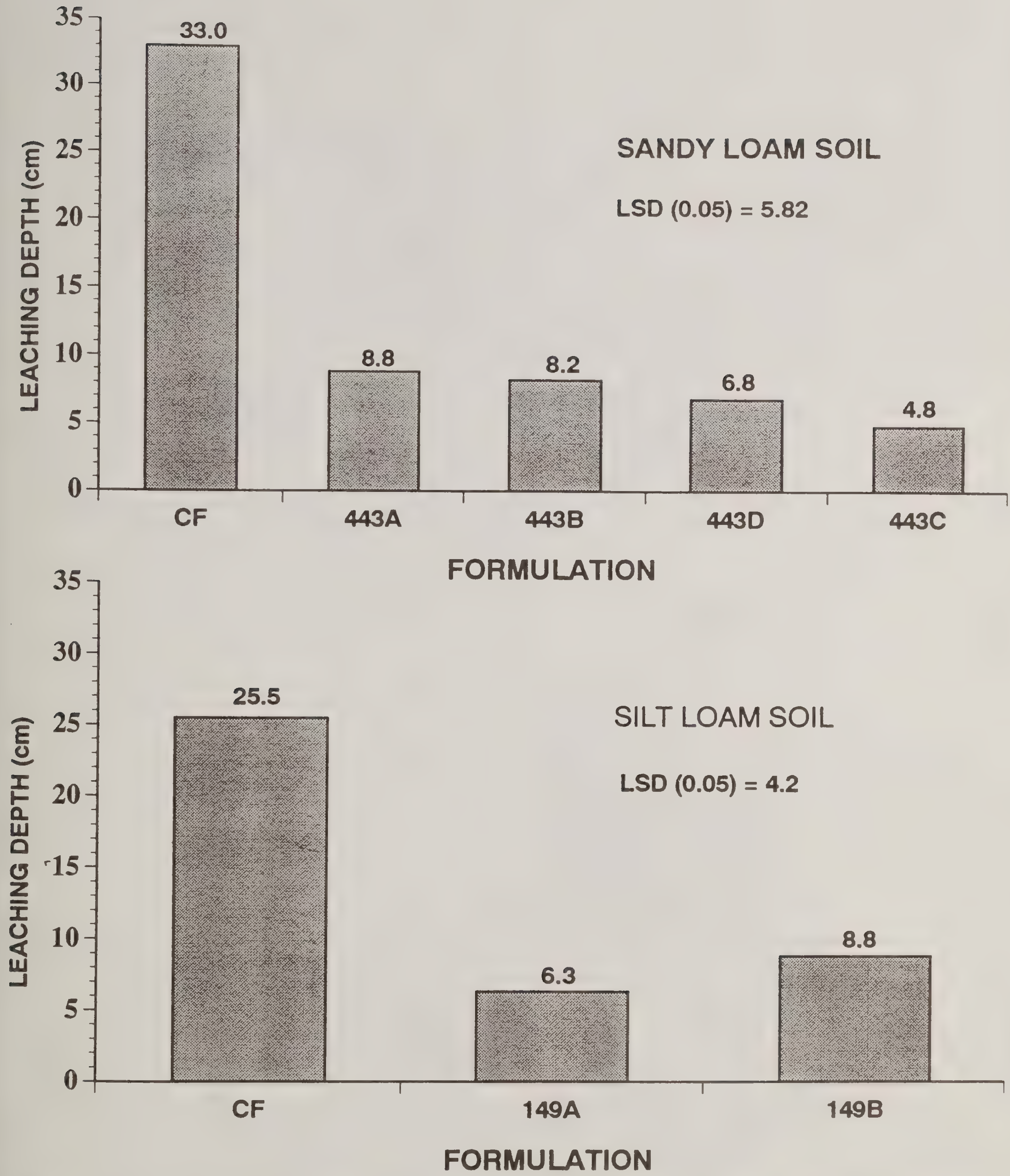

Figure 1. Atrazine leaching from commercial liquid and starch encapsulated, controlled release formulations following 75 mm simulated rainfall on silt loam and sandy loam soils. 149A, 443A and 443C passed 1.4 mm, retained by 0.85 mm screen, 149B, 443B and 443D passed 0.85 mm, retained by 0.425 mm screen. 443C and 443D were solvent washed to remove unencapsulated atrazine.

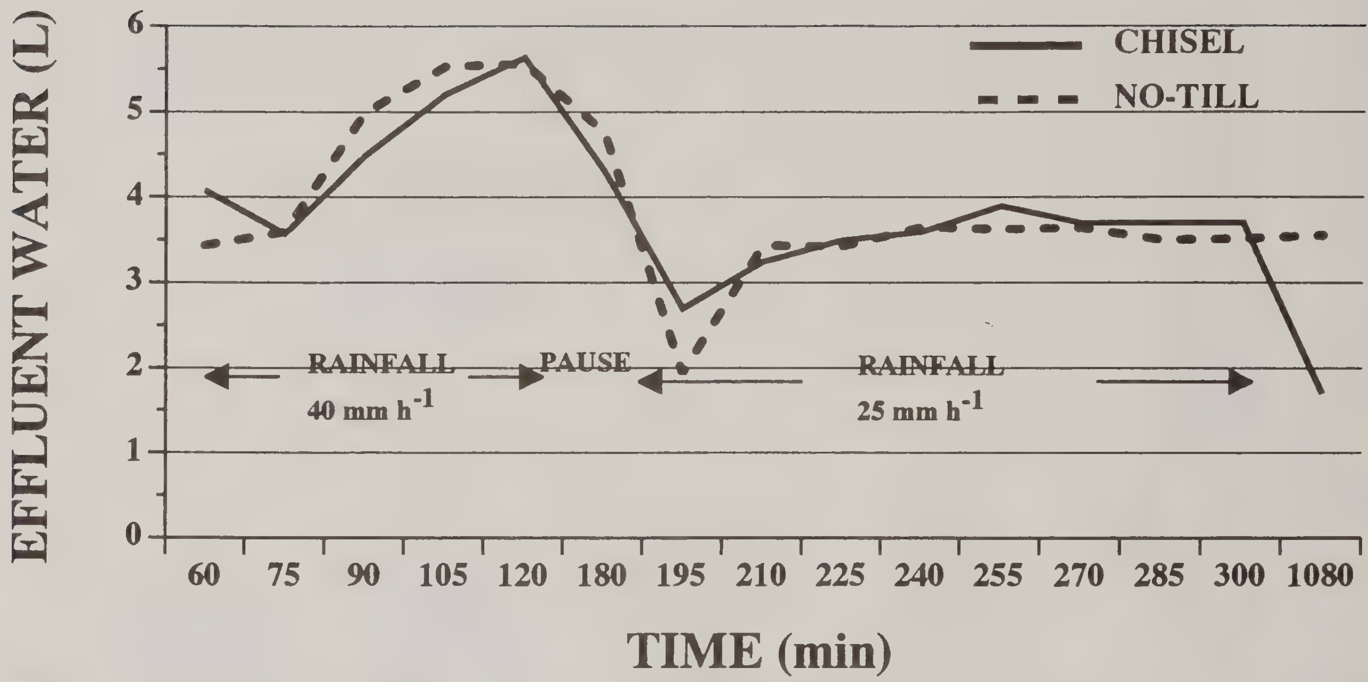

Figure 2. Effluent water collected from intact no-till and chisel plow tillage system soil blocks under simulated rainfall.

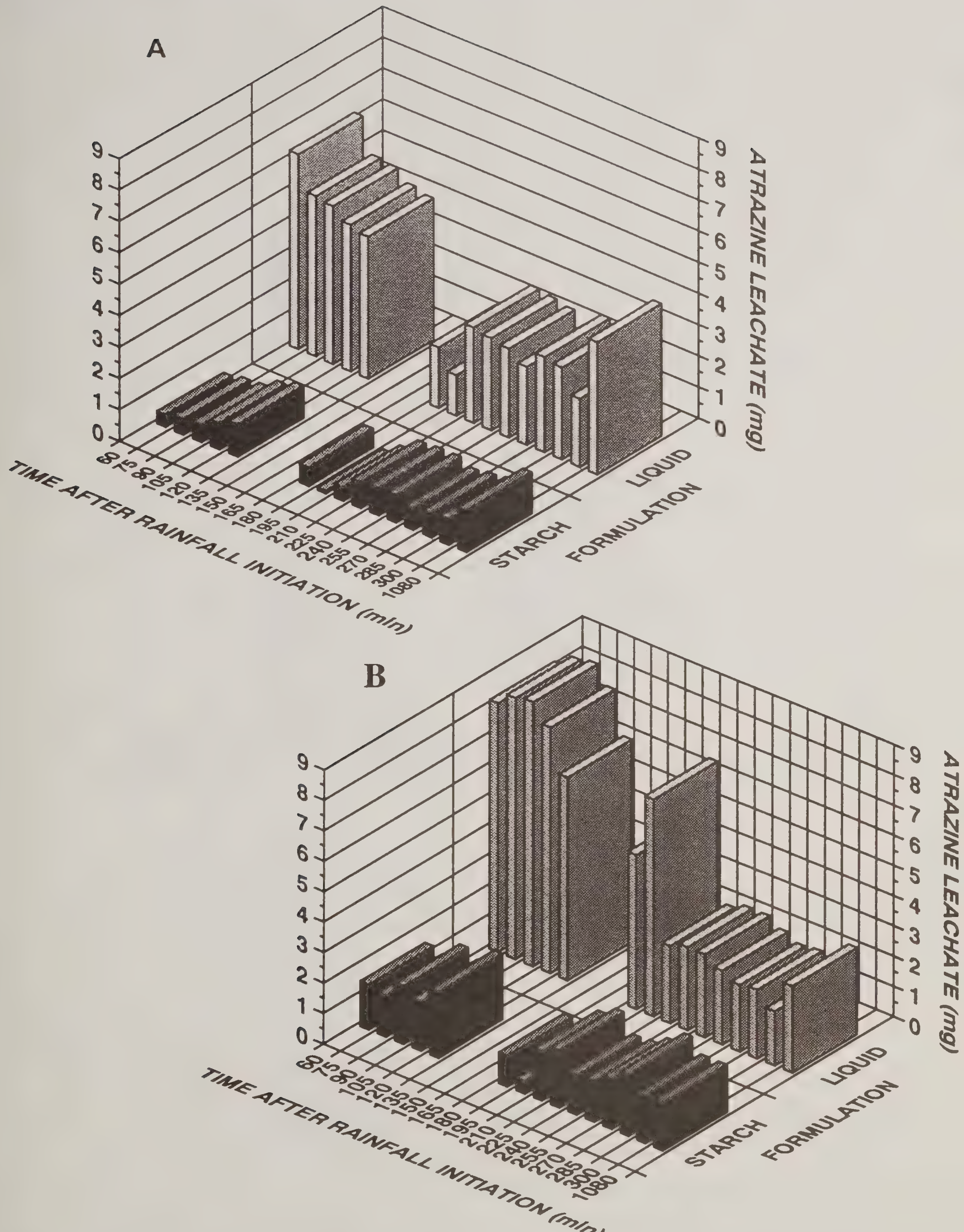

Figure 3. Atrazine in leachate from intact soil blocks treated with commercial liquid and pearl starch encapsulated atrazine formulations. A = chisel plow tillage, B = no-tillage.

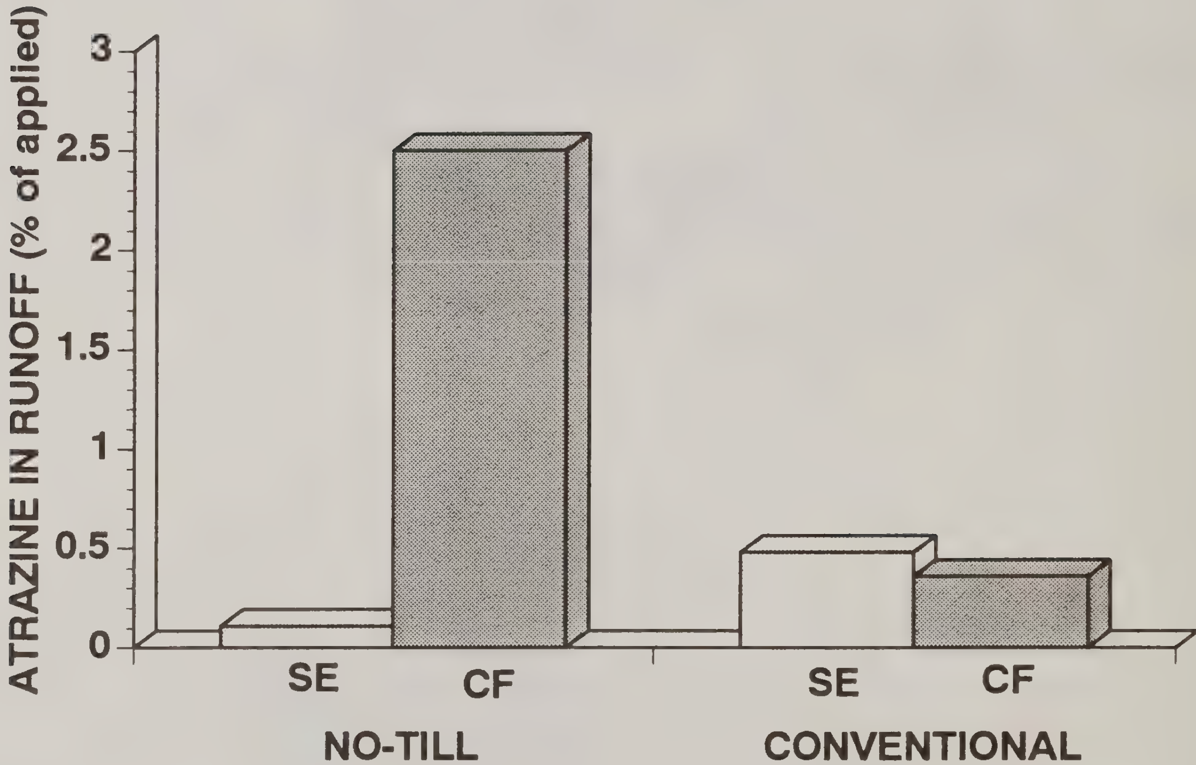

Figure 4. Atrazine loss in surface runoff water as influenced by herbicide formulation and tillage system under simulated rainfall at Lexington, IL, 1992. CF = commercial liquid, SE = pearl starch encapsulated atrazine with granules that passed 1.4 mm and were retained by 0.85 mm screen.

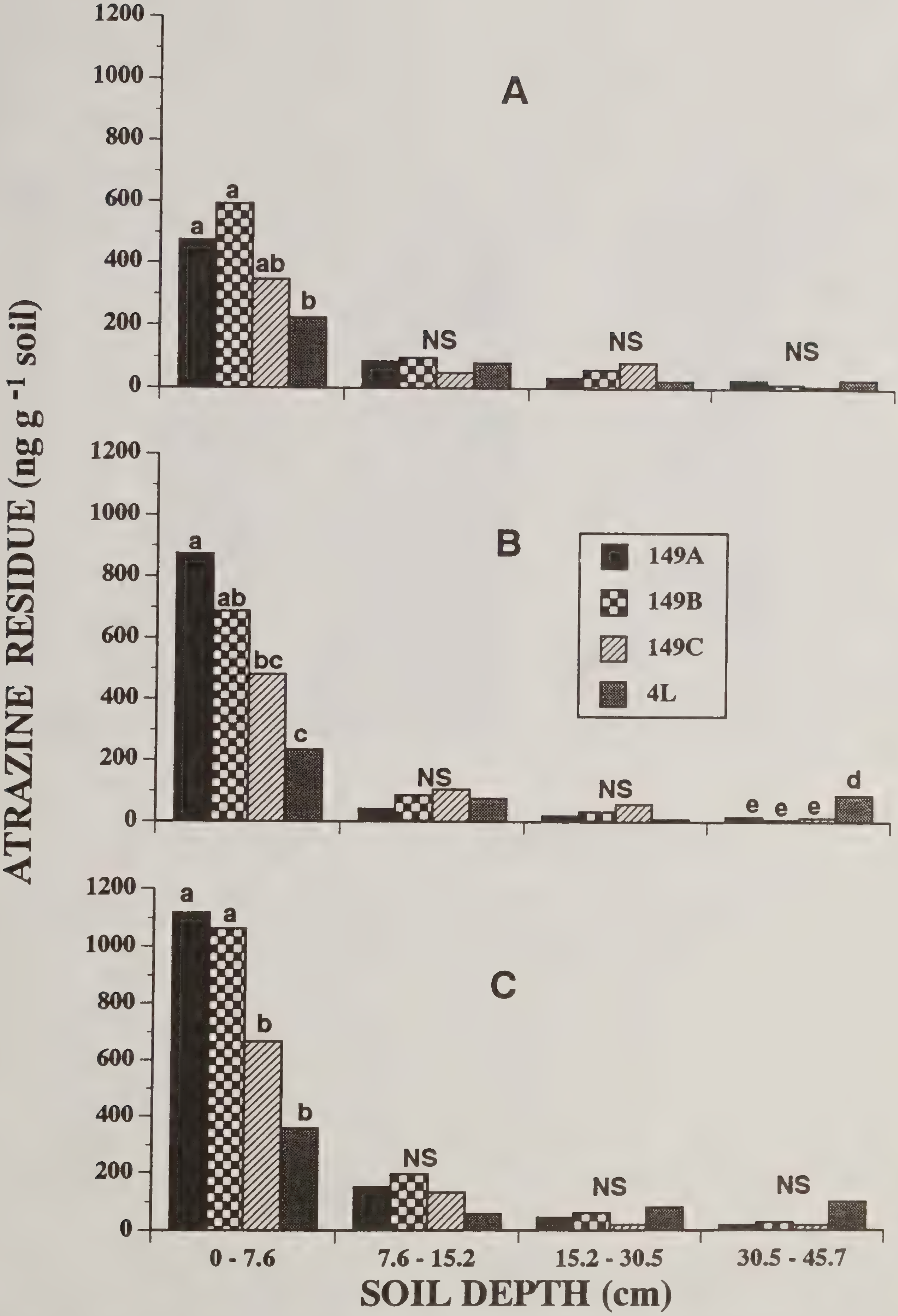

Figure 5. Atrazine residue in soil approx. 10 months after treatment with commercial liquid and pearl starch encapsulated formulations of atrazine at rates of 1.12 (A), 2.24 (B), and 3.36 (C) kg/ha. 149A passed 1.4 mm, retained by 0.85mm, 149B passed 0.85, retained by 0.425, and 149C passed 0.425 mm screens.

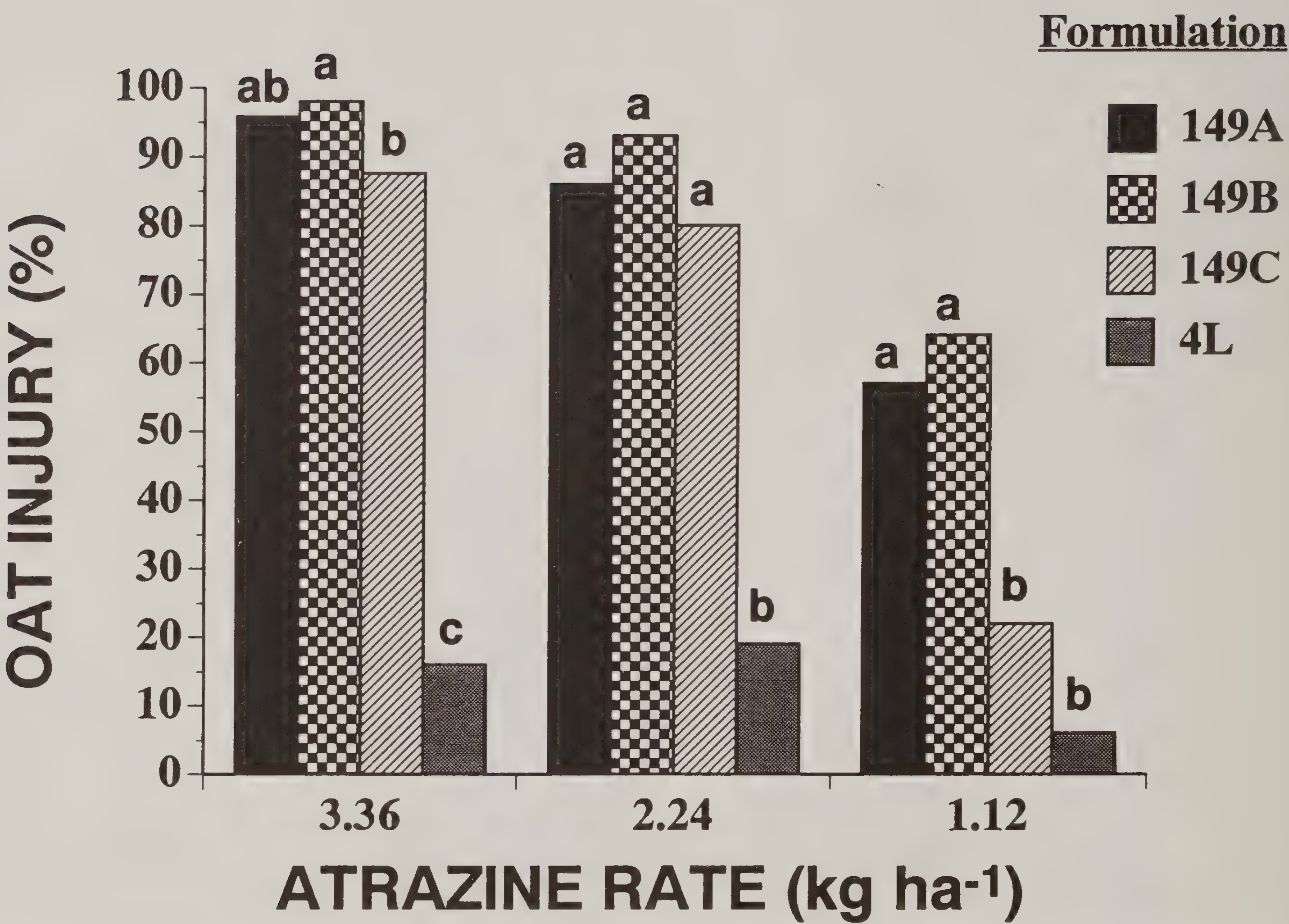

Figure 6. Atrazine injury to oats planted approx. 10 months after treatment with commercial liquid and pearl starch encapsulated formulations at three rates. 149A passed 1.4 mm, retained on 0.85 mm, 149B passed 0.85, retained on 0.425 mm, 149C passed 0.425 mm screen.

Efficacy Of Starch Encapsulated Formulations Of Herbicides

Marvin M. Schreiber and Michael V. Hickman

Regardless how environmentally safe or cost effective a new formulation may be, to be considered for adaptation, its efficacy must be equal to commercial formulation (CF) presently on the market. Herbicide efficacy is measured by the control of weeds exhibited and the resultant affects on crop yield. The following herbicides have been formulated as starch-encapsulated (SE) granules and have had extensive laboratory, greenhouse, and field testing for several years: EPTC, butylate, trifluralin, alachlor, metolachlor, and atrazine. These herbicides represent a wide range of water solubility and volatility characteristics. They have been formulated as single component granules and two or three component granules, the latter acknowledging that most preemergence herbicides are used in combinations. SE formulations of EPTC, butylate, and trifluralin have been shown to give excellent weed control under delayed incorporation and in the case of trifluralin no incorporation. Extensive field trials with SE formulations of atrazine with metolachlor or alachlor with and without dicamba gave excellent control of a wide range of weed species equal to that obtained with CF. In most cases, crop yields from plots treated with SE formulations were equal to or better than those obtained with CF under conventional and conservation tillage systems on light and heavy soils.

Introduction

Regardless of how cost effective or how environmentally safe new formulations may be, based on new technology, the final test is how effective these formulations are in real world situations. In the case of herbicides, the test is whether weed control and subsequent crop yields obtained are as good or better than commercial formulations presently on the market. This concept is somewhat ironic since there never has been a clear consensus of what constitutes commercial control.

Let us look at a hypothetical example to illustrate this point. Let us assume that a herbicide formulation can consistently control weeds at a 90% level ("commercial control") but has a high potential for environmental contamination, 80% chance. For sake of argument, a new starch-encapsulated (SE) formulation of the same herbicide can consistently control weeds at a 80-85% level, but can reduce the potential environmental contamination level to 20%. Is this trade-off worth pursuing? For whatever reason, the agricultural chemical industry has insisted that any new formulation must show efficacy equivalent to that of present commercial formulations (CF) without consideration of trade-offs. In regard to the efficacy of SE formulations, we have accepted the challenge of the standards of industry within sound statistical limits.

In terms of herbicidal action and for the purpose of this paper, efficacy means the capacity to produce weed control regardless of the loss factors that contribute to or detract from this capacity, such as by reducing losses due to leaching, volatility, and photodecomposition. The resultant effects of the weed control is the maximization of yields under the environmental conditions that prevail. Under field conditions, efficacy must be demonstrated over a range of weed species, soil textures, tillage systems, and seasons with and without moisture and temperature stresses. The data presented herewith fall well within these criteria. Table 1 and 2 list the common, trade, and chemical name of herbicides and common and scientific name of species mentioned in this paper, respectively.

Most of the efficacy studies with herbicides progressed from the laboratory to the greenhouse and finally to the field. Close collaboration was maintained with the research chemists during these periods so that formulations could be designed to fulfill the criteria desired. It cannot be stressed enough the importance of the teamwork between the research chemists and weed scientists in the ultimate design and performance of SE formulations that have been developed. All SE formulations reported in this paper are considered experimental.

Efficacy of Volatile Herbicides

The initial efficacy studies conducted with SE formulations were concerned with herbicides that required immediate incorporation into the soil because of their rapid loss due to high volatility and/or photochemical decomposition. The two main groups of herbicides were the thiocarbamates (now called carbamothioates) and the dinitroanilines represented by EPTC or butylate and trifluralin, respectively. The

Schreiber is a retired Research Leader, Hickman is a Research Agronomist. Insect and Weed Control Research, USDA-ARS-MWA, Purdue University, West Lafayette, IN 47907.

research questions addressed with these groups were: a) could SE formulations allow one to delay incorporation for some significant period of time, and b) indeed, could the need for incorporation be eliminated, both without reducing the efficacy of the herbicides.

Chlorpropham

Although our initial work was with EPTC, one SE formulation of chlorpropham was prepared for use on dodder seedlings, a species susceptible to this herbicide. The problem was that chlorpropham has a short persistence in soil and dodder because of hard seeds that germinate over time. Work by Dawson (1) indicated that the SE formulation of chlorpropham was superior to the CF and equal to a microencapsulated formulation for the control of dodder up to 5 weeks.

EPTC and Butylate

The development of SE formulations of EPTC and butylate followed the progression of SE technology, from the starch xanthates up to the jet cooking and extrusion processes. From the original xanthate formulations we were able to show initial release was adequate for weed control and slow enough for residual activity (2-4). Though not directly measured, this was undoubtedly due to control of volatility losses.

Field studies using SE formulations of EPTC and butylate made with the borate process continued to show the increased efficacy of these formulations. In 1989, SE formulations of EPTAM, ERADICANE, ERADICANE EXTRA, SUTAN and SUTAN PLUS gave excellent weed control and significant yield differences compared to their emulsifiable concentrate (EC) formulations (Tables 3 and 4). These treatments were applied when the air temperature was 32°C and the soil surface was wet from a 5 cm rainfall 3 days before treatment. Even though the formulations were incorporated within 6 h after treatment, the EC formulations lost almost all of their activity regardless of rates used. The yields of corn from plots treated with SE formulation showed no rate differences from 3.36 to 1.68 kg ha^{-1}.

These data were not surprising based on a laboratory study conducted in 1987 to compare volatility losses of SE formulations of EPTC using different processes (Figure 1). The borate process produced a formulation that was far superior than the EC. But more importantly, the jet-cooking process (the fore-runner of the extrusion process) exhibited significantly much better control of volatility loss than the borate formulation even up to 144 h sitting on a wet soil surface (5).

A field test in 1992, originally designed to study efficacy of SE extruded formulations of SUTAZINE + and ERADICANE with four times of delayed incorporation, was unsuccessful because of lack of rainfall following application. The herbicides were applied to a very dry soil and incorporations were made 0, 8, 24, and 48 h after application but the first rainfall of 1.1 cm did not occur until 10 days after application. When the weed control data was pooled over incorporation times, no significant differences in weed control were found for formulations (Table 5). Based on our previous studies and the preliminary data from similar studies in 1993, we can speculate that the SE formulations would have produced significantly better weed control than the commercial granules and EC formulations when incorporation was delayed under moist soil conditions.

The SE formulations of EPTC and butylate have also been shown to overcome accelerated thiocarbamate degradation in soil, a problem reported in several areas in the United States. It has been reported that the slow release of the active thiocarbamates from the SE formulations reduces the rapid buildup of soil microbes capable of degrading the thiocarbamates (6). The SE formulations offered significantly better control of this phenomenon than the EC or microencapsulated formulations tested.

Many volatile herbicides may be amenable to SE to control volatility losses which should increase their efficacy and safety. Recently a SE formulation of clomazone was shown to reduce volatility compared to its EC formulation (7).

Trifluralin

Trifluralin, one of the most widely used dinitroaniline herbicides, is volatile, subject to rapid decomposition by ultraviolet irradiation, and very insoluble in water. Because of these physical characteristics it was a good candidate herbicide for SE formulation. Our early work (8-9) and those of others (10) showed that application of trifluralin as a SE formulation had a lag phase before released activity was high enough to produce weed control equal to that of its EC. In both conventional tillage and no-till systems this meant early application long before soybean planting. This would make it very

adaptable for custom operators and to the farmer by reducing the workload in the spring.

Data in Table 6 indicate that early applications were necessary in conventional tillage whether surface applied or incorporated. As application times became earlier, it became apparent that in the case of SE trifluralin incorporation may not be necessary, and if so would offer an excellent herbicide for soybeans grown no-till. This was confirmed in several greenhouse and field studies. Data in Table 7 summarizes the potential for trifluralin use in no-till when formulated as a SE formulation (9).

Although pendimethylin was prepared as a SE formulation, no extensive field trials were conducted with this herbicide.

Efficacy of Herbicides Subject to Leaching

Chloroacetamides

The two most widely used chloracetamides applied to both corn and soybeans for grass control are alachlor and metolachlor. Since both compounds are water-soluble and have been reported in groundwater, they appeared to lend themselves to benefits of SE. When either herbicide was applied as a SE formulation in combination with a CF of atrazine, excellent grass control was obtained usually equal or better than CF available. In almost every case, yields of corn were significantly higher from plots treated with the SE formulation than CF. This was true whether the borate or jet-cooking process was used for SE formulation. Results were similar in conventional, chisel and no-till tillage systems.

Triazine

Although atrazine has low solubility in water, it is one of the most commonly detected herbicides in groundwater. Since most of our laboratory and field data indicate significant reduction in leaching when atrazine is formulated in starch compared to CF, it was important to evaluate efficacy of SE formulations of atrazine under field conditions. The critical question is, since atrazine has low solubility in water, are the release rates from the SE granules high enough to control weeds.

Many studies were conducted from 1988 through 1992 culminating with demonstration studies in the midwest in 1990 to 1992. Ten sites in seven states were selected to evaluate the efficacy of SE atrazine with SE formulations of alachlor or metolachlor. The sites selected represented different soil types (sands to silty clay loams), a range of weed species, diverse weather conditions, and variations of tillage systems (conventional moldboard-plow, chisel plow, and no-till).

Atrazine, alachlor, and metolachlor are herbicides that are rarely used alone in preemergence applications. Many tank mixes are approved for these herbicides. Also on the market are about 13 premixes containing atrazine, 4 containing alachlor, and 5 containing metolachlor. It logically followed that mixtures of these SE formulated herbicides be evaluated together with their CF.

SE using the extrusion process easily allows for more than one herbicide to be encapsulated in the same granule at the same time. Several two-way and three-way SE formulations containing atrazine or metribuzin were prepared and field tested.

Efficacy of Two-Way Mixtures of Separate SE Formulations

Two-way mixtures imply two herbicides applied but each formulated separately. The CF were tank mixed (unless otherwise noted) and each SE formulation was applied separately. Table 8 shows the efficacy data obtained from the midwest demonstration studies in 1990 and 1991 from applications of atrazine applied with alachlor or metolachlor. The data show the control obtained on individual weed species listing the number of sites at which the weed species was present, and the mean and range of control over sites. Control of giant foxtail (a common weedy grass in the midwest) and the small seeded broadleaf weeds such as lambsquarter and smartweed was equal between CF and SE formulations. Control of velvetleaf was variable at all sites based on the range of controls recorded. To some extent, this may be related to the depth of germination noted for velvetleaf and the concentration of atrazine at those depths. Control of common ragweed and cocklebur was usually better with the CF than with SE formulations.

The control of four species only found at one site in 1991 is shown in Table 9. Statistically, control with the SE formulations was equal or better than the CF for all species. It is interesting to note that the broadleaf species (kochia, venice mallow and jimsonweed) are all large seeded species. In the demonstration sites in 1990 and 1991, the granule size of all SE formulations was

1.4 to 0.85 mm.

In spite of the variation of weed control of some weed species, the overall yields of corn obtained in 1990 and 1991 at sites containing sandy soils (Table 10) or heavier soils (Table 11) were equal or greater with SE formulation use compared to the CF. The yields on the untreated plots give an indication of weed pressure and moisture stress during the growing season.

A study of two-way mixtures of metribuzin with alachlor or metolachlor both as CF and SE formulations in no-till soybeans was conducted in 1991. The metolachlor SE formulations were of two sizes (1.4-0.85 mm and 0.85-0.43 mm). The data shown in Table 12 indicate that in most cases the smaller the granule the better the weed control obtained with little variation in soybean yield.

Efficacy of Two or Three Herbicides in Same SE Granule

As stated earlier, the extrusion process easily allows for two or more herbicides to be entrapped in the same starch granule. The following combinations were prepared and field tested for efficacy: two-way, a) atrazine-alachlor, b) atrazine-metolachlor; three-way, a) atrazine-alachlor-dicamba, b) atrazine-metolachlor-dicamba.

In 1990, a study in conventional tilled corn was conducted using atrazine and alachlor in the same granule. Two rates and two granule sizes were used in this study. The data shown in Table 13 indicate that these herbicides in the same granule are more effective when the granule is small. However, there were no significant differences in corn yields between the CF and the SE formulations. Control of velvetleaf and jimsonweed, two large seeded weeds, was variable as noted in the extensive demonstration studies reported earlier.

Atrazine is a weak herbicide for velvetleaf control even in the CF available. When used in a SE formulation, the rate of release appears more borderline. Could the addition of an excellent broadleaf control herbicide such as dicamba bring the control up to that of the CF? Dicamba is a premix in about 12 commercial herbicides now on the market. In 1992, we investigated the efficacy of two-way combinations of atrazine and alachlor as individual CF and SE formulations and as a combined mixture in the same granule. These formulations were compared to three-way mixtures of atrazine, alachlor, and dicamba each as a CF tank mix and all in the same SE granule. This study was conducted in conventional tilled corn using the larger SE granules, 1.4 to 0.85 mm.

The results of this study are shown in Table 14 and indicate that the addition of dicamba, whether in the granule or in the tank mix, increases the efficacy of control of velvetleaf and ivyleaf morningglory. The efficacy of the SE formulation was equal to that of the CF and the corn yields were similar.

A similar study in 1992 was conducted in no-till corn using metolachlor instead of alachlor and two granule sizes. The results shown in Table 15 indicate similar weed control as noted in conventional tilled corn with lower corn yields. The extremely low rainfall received in May and June of 1992 affected the weed control and corn yields more in the no-till than in the conventional tilled corn.

Relationship of Granule Size and % A.I. Encapsulated on Efficacy

Most of the SE formulations of atrazine, alachlor, and metolachlor used in these studies contained approximately 10% a.i. Since uniform distribution of granules on the soil surface is critical for effective control, there is a significant relationship between size of granules and a.i. This relationship changes slightly with different physical characteristics of the herbicides. As an example, in the case of EPTC, a highly volatile herbicide, it is very likely that a granule containing 25% a.i. would give adequate distribution with a granule size of 1.4 mm. The sphere of influence of each granule should give enough overlap for good weed control. In the case of atrazine, which is not highly volatile or water-soluble, its sphere of influence from individual granules is small and a 25% a.i. formulation would require a very fine granule for adequate control. We believe that the a.i. percentages and granule sizes we have worked with are close to the most desirable levels for each herbicide studied.

Summary

Our data indicate that SE formulations can be efficacious based on weed control and crop yield. Volatile herbicides and those subject to photo-decomposition are more efficient in SE formulations than CF now on the market, even under adverse weather conditions. Combination of herbicides in the same SE granule can broaden the spectrum of weed

control for soil applied herbicides in light and heavy soils and under various tillage systems. Coupled with economics of twin-screw extrusion and the ability to reduce environmental impact, SE offfers an excellent new technology for herbicide formulations.

References

1. Dawson, J.H. 1980. U.S. Dept. of Agriculture, Agriculture Research Service, Prosser,Washington, personal communication.

2. Schreiber, M.M., B.S. Shasha, M.A. Ross, P.L. Orwich, and Y.W. Edgecomb. 1978. Efficacy and rate of release of EPTC and butylate from starch encapsulated formulations under greenhouse conditions, Weed Science 26:679-686.

3. Schreiber, M.M., and M.D. White. 1980. Granule structure and rate of release with starch-encapsulated thiocarbamates, Weed Science 28:685-690.

4. Schreiber, M.M., and M.D. White. 1980. Effect of formulation technology on the release of starch encapsulated EPTC. Proceedings British Crop Protection Conference-Weeds. 15:225-229.

5. Schreiber, M.M., M.D. White, R.E. Wing, D. Trimnell, and B.S. Shasha. 1988. Bioactivity of controlled-release formulations of starch-encapsulated EPTC, Journal Controlled Release 7: 237-242.

6. Hall, F.R., J.F. Reed, and D.Trimnell. 1989. Preemergence application of herbicides encapsulated in starch for overcoming accelerated thiocarbamate degradation. Proc. Intern. Symp. Control. Rel. Bioact. Mater. 16:424-425.

7. Mervosh T.L., E.W. Stoller, and R.E. Wing. 1993. Granular formulations reduce clomazone volatility from soil surface, Weed Science Society of America Abstracts 35:81.

8. White, M.D., and M.M. Schreiber. 1984. Herbicidal activity of starch-encapsulated trifluralin, Weed Science 32:387-394.

9. Schreiber, M.M., M.D. White, and B.S. Shasha. 1987. Efficacy of controlled-release formulations of trifluralin in no-till soybeans (***Glycine max***), Weed Science 35:407-411.

10. Coffman, C.B., W.A. Gentner, and B.S. Shasha. 1984. Herbicidal activity of controlled release formulations of trifluralin, Indian Journal of Agricultural Science 54:117-122.

Table 1. Common, trade, and chemical names of herbicides mentioned in this paper

Common name	Trade name	Chemical name
Alachlor	Lasso	2-chloro-*N*-(2,6-diethylphenyl)-*N* (methoxymethyl) acetamide
Atrazine	"Many"	6-chloro-*N*-ethyl-*N*'-(1-methylethyl)-1,3,5-triazine-2,4--diamine
Butylate	Sutan	*S*-ethyl bis(2-methylpropyl) carbamothioate
	Sutan+	butylate+R-29148 3-(dichloroacetyl)-2,2,5-trimethyloxazolidine
Chloramben	Amiben	3-amino-2,5-dichlorobenzoic acid
Chlorpropham	Furloe	l-methylethyl 3-chorophenylcarbamate
Clomazone	Command	2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone
Dicamba	Banvel	3,6-dichloro-2-methoxybenzoic acid
EPTC	Eptam	*S*-ethyl dipropyl carbamothioate
	Eradicane	EPTC+dichlormid (2,2-dichloro-*N*-*N*-di-2-propenylacetamide)
	Eradicane extra	EPTC+R-29148+dietholate (0,0-diethyl 0-phenyl phosphorothioate)
Metolachlor	Dual	2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-l-methylethyl) acetamide
Metribuzin one	Sencor,lexone	4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4- triazi-5(4H)-
Norflurazon	Zorial	4-chloro-5-(methylamino)-2-(3-trifluoroethyl)phenyl)-3(2H)-pyridazinone
Pendimethalin	Prowl	*N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine
Simazine	"Many"	6-chloro-*N*,*N*' -diethyl-1,3,5-triazine-2,4-diamine
Trifluralin	Treflan	2,6-dinitro-*N*,*N*-dipropyl-4-(trifluoromethyl)benzenamine
	<u>Premixes</u>	
Bicep	Atrazine+metolachlor	CIBA-GEIGY
Bullet	Atrazine+alachlor	Monsanto
Sutazine	Atrazine+butylate	ICI americas

Table 2. Common and scientific names of weed and crop species mentioned in this paper

Common name	Scientific name
Dodder	*Cuscuta campastris* L.
Giant foxtail	*Setaria faberi* Herrm.
Ivyleaf morningglory	*Ipomoea hederacea* (L.) Jacq.
Jimsonweed	*Datura stramonium* L.
Common lambsquarters	*Chenopodium album* L.
Kochia	*Kochia scoparia* (L.) Schrad.
Venice mallow	*Hibiscus trionum* L.
Pennsylvania smartweed	*Polygonum pensylvanicum* L.
Redroot pigweed	*Amaranthus retroflexus* L.
Common ragweed	*Ambrosia artemisiifolia L.*
Common cocklebur	*Xanthium strumarium* L.
Longspine sandbur	*Cenchrus longispinus* (Hack.) Fern.
Velvetleaf	*Abutilon theophrasti* medic.
Corn	*Zea mays* L.
Soybean	*Glycine max* (L.) Merr.

Table 3. Effects of commercial (EC) and starch encapsulated (SE) formulations and rates of EPTC on corn yields, 1989

Herbicide (formulation)	Rate	Yield [a]
	kg ha^{-1}	
EPTAM (EC)	1.68	5688 abc
EPTAM (EC)	3.36	4728 abc
EPTAM (SE)	1.68	9237 def
EPTAM (SE)	3.36	9664 ef
ERADICANE (EC)	1.68	4365 ab
ERADICANE (EC)	3.36	5004 abc
ERADICANE (SE)	1.68	9607 ef
ERADICANE (SE)	3.36	10272 f
ERADICANE EXTRA (EC)	1.68	3694 a
ERADICANE EXTRA (EC)	3.36	4189 ab
ERADICANE EXTRA (SE)	1.68	8579 def
ERADICANE EXTRA (SE)	3.36	9218 def
Untreated check	—	3023 a
Handweeded check	—	9858 ef

[a]Means within yield column followed by the same letter do not differ significantly based on Fisher's Protected LSD (0.05).

Table 4. Effects of commercial (EC) and starch encapsulated (SE) formulations and rates of butylate on corn yields, 1989

Herbicide (formulation)	Rate	Yield [a]
	kg ha^{-1}	
SUTAN (EC)	1.68	2916 a
SUTAN (EC)	3.36	4490 ab
SUTAN (SE)	1.68	6578 bcd
SUTAN (SE)	3.36	9676 ef
SUTAN + (EC)	1.68	5437 abc
SUTAN + (EC)	3.36	5186 abc
SUTAN + (SE)	1.68	7306 cde
SUTAN + (SE)	3.36	8667 def
Untreated check	—	3023 a
Handweeded check	—	9858 ef

[a]Means within yield column followed by the same letter do not differ significantly based on Fisher's Protected LSD (0.05).

Table 5. Efficacy of sutazine + and eradicane formulations incorporated in conventional tilled corn, 1992

Herbicide (formulation)	Rate	Control by species [a] Giant foxtail	Velvet-leaf	Jimson-weed
	kg ha^{-1}	%		
Sutazine + 24G (CF)	6.3	96	76	82
Sutazine + 24 SE	6.3	96	60	62
Sutazine + EC	6.3	96	76	92
Eradicane 25 G (CF)	4.7	99	96	92
Eradicane 27 SE	4.7	82	93	87
Eradicane 15 SE	4.7	99	97	90
Eradicane EC	4.7	99	97	86

[a]No signifcant differences within any herbicide and weed species.

Table 6. Effects of time of application and placement of commercial (CF) and starch-encapsulated (SE) formulations of trifluralin on soybean yields (1982) (trifluralin rate 1.7 kg ha^{-1})

Application		Yields [ab]		
Time	Placement	SE	EC	Untreated
		kg ha^{-1}		
12-7-81	Incorporated	2950 aA	2460 bB	2010 aC
12-7-81	Surface	2990 aA	2160 bB	1850 aC
4-19-82	Surface	2850 aA	2260 bB	2320 aB
5-10-82	Surface	2960 aA	2160 bB	1900 aB
6-21-82[c]	Incorporated	2610 aB	3120 aA	1960 aC

[a]Values within column followed by the same lower case letter are not significantly different according to Duncan's Multiple Range Test (0.05).
[b]Values within a row followed by the same capital letter are not significantly different according to Duncan's Multiple Range Test (0.05).
[c]Date of planting.

Table 7. Effect of commercial (CF) and starch encapsulated (SE) formulations of trifluralin and time of application on no-till soybean yields (1985) (trifluralin rate 1.4 kg ha^{-1})

Trifluralin formulation	Yield [ab] Application time	
	3-29-85	5-7-85
	kg ha^{-1}	
CF	2165 bA	3107 aB
SE	3262 aA	3329 aA
Untreated check	2381 bA	2340 bA

[a]Means within a yield column followed by same lower case letter are not significantly different according to Duncan's Multiple Range Test (0.05).
[b]Means with a row followed by same capital letter are not significantly different according to Duncan's Multiple Range Test (0.05).

Table 8. Efficacy of commercial (CF) and starch encapsulated (SE) formulations of atrazine (AT), alachlor (AL), and metolachlor (ME) in 1990 and 1991 field studies

Weed Species Herbicide formulation	1990 Sites	1990 Mean weed control	1990 Range of weed control	1991 Sites	1991 Mean weed control	1991 Range of weed control
	No.	%		No.	%	
Giant Foxtail						
AT (CF) + AL (CF)	8	93	64-100	9	94	59-100
AT (SE) + AL (SE)	8	89	78-99	9	90	61-100
AT (CF) + ME (CF)	8	94	90-100	9	92	46-100
AT (SE) + ME (SE)	8	90	77-98	9	79	9-100
Velvetleaf						
AT(CF) +AL(CF)	9	81	0-83	8	71	0-100
AT (SE) + AL (SE)	9	59	1-88	8	56	0-95
AT(CF) + ME (CF)	9	82	0-100	8	78	0-100
AT(SE) + ME (SE)	9	65	0-89	8	50	0-96
Lambsquarter						
AT (CF) + AL (CF)	5	99	96-100	4	99	99-100
AT (SE) + AL (SE)	5	99	99-100	4	99	97-100
AT (CF) + ME (CF)	5	99	99-100	4	99	99-100
AT(SE) + ME (SE)	5	96	95-100	4	96	87-100
Smartweed						
AT (CF) + AL (CF)	3	97	91-100	2	96	93-100
AT (SE) + AL (SE)	3	93	84-100	2	95	91-100
AT (CF) + ME (CF)	3	95	86-100	2	97	95-100
AT (SE) + ME (SE)	3	92	85-100	2	96	92-100
Common Ragweed						
AT (CF) + AL (CF)	2	93	86-100	1	89	-
AT (SE) + AL (SE)	2	82	73-90	1	78	-
AT (CF) + ME (CF)	2	94	83-99	1	50	-
AT (SE) + ME (SE)	2	60	84-75	1	78	-
Cocklebur						
AT (CF) + AL (CF)	2	92	85-99	1	92	-
AT (SE) + AL (SE)	2	72	69-74	1	58	-
AT (CF) + ME (CF)	2	86	74-98	1	94	-
AT (SE) + ME (SE)	2	73	56-89	1	60	-

Table 9. Efficacy of commercial (CF) and starch encapsulated (SE) formulations of atrazine (AT), alachlor (AL), and metolachlor (ME) at single sites in 1991

Herbicide formulation	Control by Species			
	Sandbur	Kochia	Venice mallow	Jimson-weed
AT(CF) + AL(CF)	73	100	97	82
AT(SE) + AL(SE)	64	100	88	65
AT(CF) + ME(CF)	82	0	98	82
AT(SE) + ME(SE)	91	100	88	82

Table 10. Effect of commercial (CF) and starch encapsulated (SE) formulations of atrazine (AT), alachlor (AL), and metolachlor (ME) on corn yields on sandy soils in 1990 and 1991

Herbicide formulation	1990			
	Kilbourne IL	Wanatah IN	Westport MN	
	$kg\ ha^{-1}$			
AT(CF) + AL(CF)	4580	9660	5080	
AT(SE) + AL(SE)	2760	9660	5080	
AT(CF) + ME(CF)	3830	10280	4890	
AT(SE) + ME(SE)	3260	9280	5020	
Untreated check	1570	9530	3890	
LSD(0.05)	815	1190	380	
	1991			
	Kilbourne IL	Wanatah IN	Westport MN	Madrid NE
	$kg\ ha^{-1}$			
AT(CF) + AL(CF)	6710	5520	7460	11100
AT(SE) + AL(SE)	4890	6150	6960	11040
AT(CF) + ME(CF)	5330	6080	7650	6150
AT(SE) + ME(SE)	7530	5580	7150	12100
Untreated check	3640	5080	0	10790
LSD(0.05)	3260	1000	750	1130

Table 11. Effect of commercial (CF) and starch encapsulated (SE) formulations of atrazine (AT), alachlor (AL), and metolachlor (ME) on corn yields on silty loam and clay loam soils in 1990 and 1991

Herbicide (formulation)	W. Laf. IN	Urbana IL	Ames IA	Rosemount MN
1990	kg ha^{-1}			
AT(CF) + AL(CF)	9280	8340	6520	7900
AT(SE) + AL(SE)	10600	8460	6840	7530
AT(CF) + ME(CF)	10850	8400	7460	7960
AT(SE) + ME(SE)	9780	6650	5330	7340
Untreated check	7210	6270	4330	250
LSD (0.05)	1230	1630	NS	440
1991				
AT(CF) + AL(CF)	7710	3760	4580	9970
AT(SE) + AL(SE)	6400	3450	3890	9340
AT(CF) + ME(CF)	7020	3070	4200	10030
AT(SE) + ME(SE)	6900	3140	4890	9160
Untreated check	3760	2822	4140	5800
LSD (0.05)	940	NS	NS	820

Table 12. Efficacy of commercial and starch encapsulated (SE) formulations of alachlor(AL) and metolachlor (ME) with metribuzin (MET) in no-till soybeans, 1991

Treatments (formulation)	Granule sizes	Rates	Control by Species [a] Giant foxtail	Velvet-leaf	Jimson-weed	Soybean yield
	mm	kg ha^{-1}	%			kg ha^{-1}
ME(EC)+MET(EC)		2.24+0.56	84 ab	53 b	82 a	2489
ME(EC)+MET(EC)		2.80+0.56	94 ab	68 b	60 a	2871
ME(SE) +MET(SE)	1.4-0.85+0.85-0.43	2.24+0.56	80 ab	79 ab	95 a	2662
ME(SE)+MET(SE)	1.4-0.85+0.85-0.43	2.80+0.56	98 ab	80 ab	97 a	2484
ME(SE)+MET(SE)	0.85-0.43+0.85-0.43	2.24+0.56	98 ab	76 ab	68 a	2507
ME(SE)+MET(SE)	0.85-0.43+0.85-0.43	2.80+0.56	100 a	85 ab	92 a	2613
AL(SE)+MET(SE)	1.4-0.85+0.85-0.43	2.24+0.56	90 ab	80 ab	55 a	2441
AL(SE)+MET(SE)	1.4-0.85+0.85-0.43	2.80+0.56	57 b	72 b	94 a	2542
AL(SE)+MET(SE)	0.85-0.43+0.85-0.43	2.24+0.56	82 ab	71 b	69 a	2698
AL(SE)+MET(SE)	0.85-0.43+0.85-0.43	2.80+0.56	94 ab	95 a	68 a	2613
LASSO II+MET(SE)	0.85-0.43	2.80+0.56	100 a	83 ab	85 a	2642
Untreated check			—	—	—	1978
LSD (0.05)						290

[a]Means within column of a weed species followed by the same letter do not differ significantly based on Fisher's Protected LSD (0.05).

Table 13. Effect of granule size and rate of application on weed control and corn yield from starch encapsulated atrazine (AT) and alachlor in same granule under conventional tilled corn, 1990

Granule size	Rate AT-AL	Giant foxtail	Velvet-leaf	Redroot pigweed	Lambs-quarter	Jimson-weed	Yield [b]
mm	kg ha^{-1}	%					kg ha^{-1}
Commercial[a]	1.68+2.80	97	56	97	100	82	10000 c
Commercial	2.24+3.70	99	84	100	100	86	9730 c
1.4-0.85	1.68-2.80	75	12	95	100	27	9580 bc
1.4-0.85	2.24-3.70	88	30	99	100	48	8800 ab
0.85-0.43	1.68-2.80	92	16	94	100	59	9570 bc
0.85-0.43	2.24-3.70	97	45	100	100	80	9210 bc
Untreated check		—	—	—	—	—	8150 a
LSD (0.05)		17	23	9	NS	40	

[a]Commercial formulations of atrazine and alachlor was premixed BULLET.
[b]Means within yield column followed by same letter do not differ significantly based on Fisher's Protected LSD Test.

Table 14. Effects of commercial (CF) and starch encapsulated (SE) formulations of atrazine (AT), alachlor (AL), and dicamba (DC) on weed control and corn yields in conventional tillage, 1992 rates kg ha^{-1}. AT: 2.2, AL: 3.3, DC: 0.4. granule size: 1.4-0.85 mm

Herbicide formulations	Control by species					
	Giant foxtail	Velvet-leaf	Ivy leaf morning glory	Lambs-quarter	Redroot pigweed	Yield
	%					kg ha^{-1}
AT(CF)+AL(CF) [a]	96	94	95	96	96	11090
AT(SE)+AL(SE) [b]	87	58	83	75	90	10330
AT-AL(SE)	82	45	63	90	94	10430
AT(CF)+AL(CF)+DC(CF)	98	96	97	98	98	11040
AT-AL-DC(SE)	92	93	93	94	94	11080
Untreated check	--	--	--	--	--	9310
LSD (0.05)	7	14	11	14	5	920

[a]All commercial formulations were liquid and tank mixed.
[b]Starch encapsulated mixtures with a + sign were separate granule formulations, with a - sign indicates component herbicides in the same granule.

Table 15. Effects of commercial (CF) and starch encapsulated (SE) formulations of atrazine (AT), metolachlor (ME), and dicamba (DC) on weed control and corn yields in no-till, 1992. Rates kg ha^{-1}; AT:2.8, ME:3.2, DC:0.4

Herbicide formulation	Granule size	Control by species: Giant-foxtail	Control by species: Velvet-leaf	Yield
	mm	%	%	kg ha^{-1}
AT(CF)+ME(CF)	--	96	68	6370
AT(SE)+ME(SE)	1.4-0.85	96	74	6980
AT(SE)+ME(SE)	0.85-0.43	97	70	7280
AT-ME(SE)	1.4-0.85	95	70	7040
AT-ME(SE)	0.85-0.43	96	79	6940
AT(CF)+ME(CF)+DC(CF)	--	98	97	6620
AT-ME-DC(SE)	1.4-0.85	95	90	6840
AT-ME-DC(SE)	0.85-0.43	97	80	5790
Untreated check	--	--	--	6060
LSD (0.05)	NS	14.5	NS	

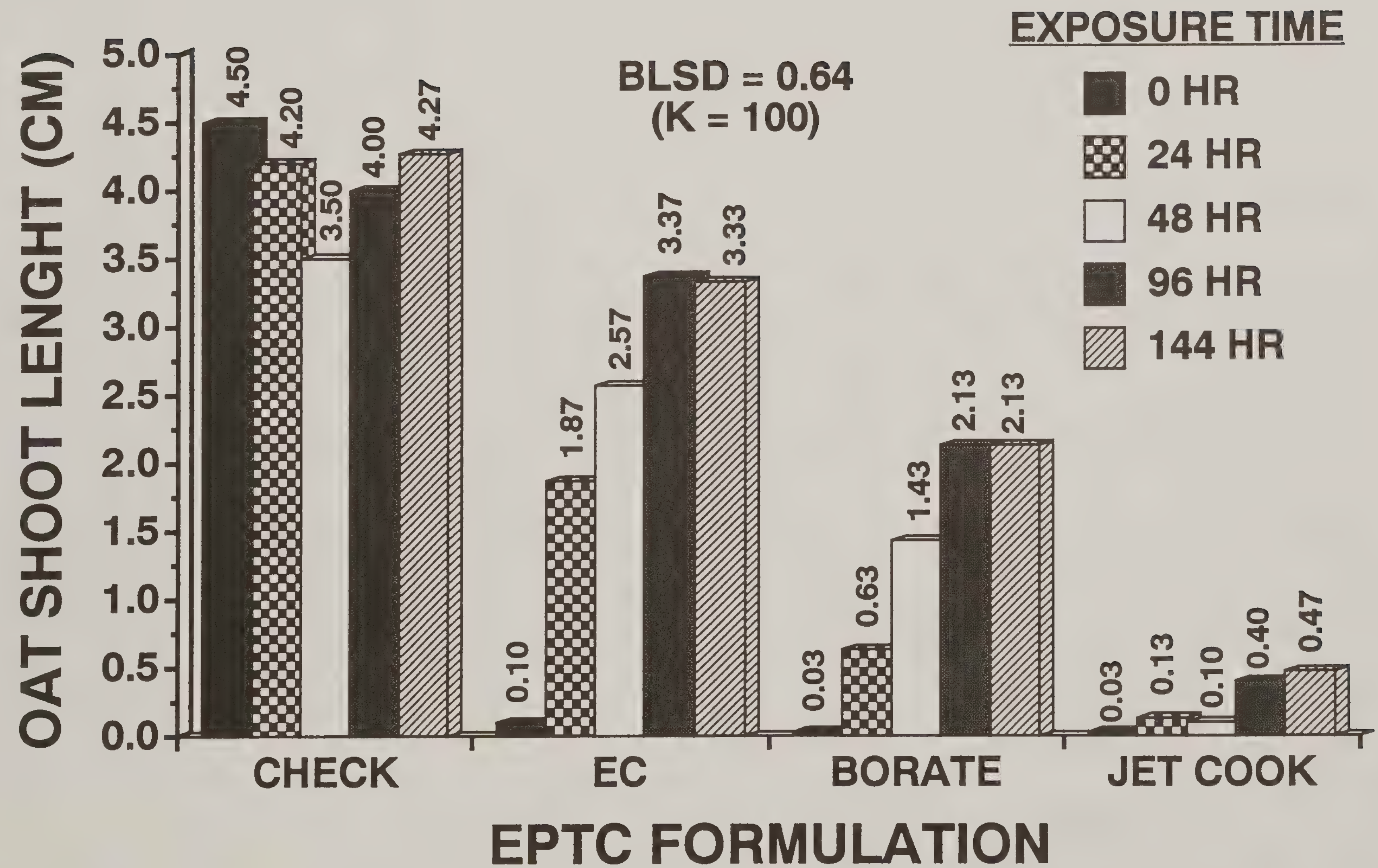

Figure 1. Oat shoot bioassays of EPTC starch-encapsulated formulations exposed on a wet soil surface up to 144 hours.

Starch Encapsulation of Microbial Pesticides for Sustained Activity

Michael R. McGuire and Baruch S. Shasha

Many environmental and biological factors act to reduce the insecticidal potential of microbial pesticides. Each of these factors can be addressed through formulation. Over the past several years, we have investigated formulation of microbial insecticides within starch matrices. While chemical pesticides have been encapsulated in starch for many years, the biological nature of microbial insecticides has prohibited the use of the harsh chemicals or extreme pH necessary to ensure gelatinization of the starch and subsequent entrapment of active ingredient. Pregelatinized starches and flours have facilitated formulation of microbial pesticides. Three distinct types of starch formulations have been developed: a sprayable and two granular baits. The sprayable formulation is composed of a pre-mixed combination of pregelatinized cornstarch or pregelatinized flour and sucrose that can be tank mixed at solids rates of 2-6%. Bioassays of cotton or cabbage leaf tissue treated with the sprayable formulations demonstrated increased residual activity of *Bacillus thuringiensis kurstaki* (Btk) after simulated (greenhouse) or actual (field) rainfall. Similarly, experiments with small field plots of cabbage treated with the sprayable formulations demonstrated efficacy similar to that of conventional chemical insecticides. The two types of granular formulations are a conventional type granule which remains discrete through wet and dry periods and an adherent granule which will slightly dissolve and remain stuck to leaf tissue upon contact with water. Following drying, the granule remains tightly attached to the leaf surface. The granular formulations have been tested extensively against European corn borer in whorl stage corn. Sunlight screens incorporated within the granules significantly increased residual activity of Btk when granules were exposed to direct sunlight. Under field conditions, feeding stimulants allowed a decrease in Btk concentration without significant loss of insect control. Work with these formulations is continuing with the addition of viruses and fungi to our research program. Clearly, improvements to formulations of microbial pesticides will enhance the acceptance and reliability of these important pest control tools.

McGuire is a Research Entomologist and Shasha is a Research Chemist, National Center for Agricultural Utilization Research, USDA-ARS, Peoria, IL 61604.

Introduction

Chemical pesticides have long been used to control insects of agricultural and medical importance. In the U.S. alone, more than 300 million pounds of active agent are applied annually. Recent acknowledgment of environmental and health concerns associated with the wide scale use of chemical pesticides, however, will lead to a shift towards the use of more health and environment friendly active ingredients. Our challenge, now, is to integrate these new agents into a feasible and economical program of pest control.

Microorganisms have long been known to cause disease and death in insects. Epizootics of these organisms in populations of insects are often very striking as virtually every insect in a naturally occurring population may be dead or dying late in the infection cycle. Unfortunately, however, these epizootics usually occur late in the population cycle of the insect after economic damage to the crop has occurred. Further, epizootics occur sporadically, are dependent on environmental conditions and are extremely difficult to predict. Over the past 100 years, attempts have been made to use these disease agents in a proactive way; i.e., introduce the pathogens into field populations of insects to cause an epizootic and, thus, control the population (1). One method of introduction involves the infection of insects in the laboratory followed by mass release of the infected insect into field populations of the same species. Pathogens released in this inoculative manner then should slowly spread through the population and eventually bring the insect under control. The other major strategy involves the mass production of the pathogen and direct application to a damaging population of insects. This inundative approach requires formulating the pathogen such that it survives in the environment until it is fed upon by the target species.

The discovery of *Bacillus thuringiensis* Berliner subsp. *kurstaki* (Btk), a spore forming soil bacterium lethal to insects, has led to a great many products (2). Btk is easy to mass produce and has a relatively resistant spore and protein crystal that are responsible for insect mortality. Individual strains of Btk have small host ranges and fit well into integrated pest management programs. However, Btk presents a challenge to formulation scientists. It is a particulate and must be suspended uniformly through a spray mixture. Also, Btk is a living organism and formulations must be designed to protect it from breaking down in the environment before it is fed upon by the target insect.

Sunlight, especially that portion in the ultraviolet range, denatures spores (3) and crystals (4), and rainfall washes the particulates from the surfaces of treated plants. Further, Btk is not especially palatable to an insect; the insect may feed on contaminated foliage for only a short time without ingesting a lethal dose of Btk. If the insect then encounters unsprayed plant tissue, it may feed and recover from the sublethal infection. These factors have acted to inhibit mass use of this valuable pest control tool.

Over the past few years, we have been working to adapt starch encapsulation technology for formulation of Btk. However, due to the biological nature of Btk, past starch formulations involving high heat or harsh chemicals were not acceptable. The availability of cold water dispersible pregelatinized starches have allowed formulation of Btk in protective, rainfast, and palatable formulations. Three major types of starch formulations have been developed for Btk: two types of granules and a sprayable.

Granular Formulations of *Bacillus thuringiensis*

Non-Adherent Formulations

Pregelatinized cornstarches such as Miragel (A.E. Staley, Inc., Decatur, IL), upon contact with water at room temperature will form a gelled mass. Using a ratio of 3 parts water to 2 parts Miragel, Dunkle and Shasha (5) developed a process to macro-encapsulate Btk in a cross-linked starch matrix. This matrix was ground to the desired particle size, usually in the 16-40 mesh range. The granules flow easily through standard on-farm granular applicators and are effective for control of the European corn borer.

These granules have been thoroughly tested over the past few years against the European corn borer, *Ostrinia nubilalis* (Lepidoptera: Pyralidae). To determine if the granules were palatable to corn borer larvae, a bioassay was developed (6) to test the effectiveness of various possible feeding stimulants incorporated within the starch granules. The assay involved placing two types of granules at opposite sides of a round plastic petri dish that had been lined on the bottom with a plaster of Paris and charcoal mixture. Larvae (less than 12 h old) were then placed in the middle of the dish, the dish was capped and held for 16-24 h in the dark, and then quickly frozen. Dishes were opened and the number of larvae at each site was recorded. Although many additives were tested, the following conclusions were drawn: First, starch, by itself is not highly preferred by larvae, especially when tested against a corn leaf disk or other feeding stimulant; second, individual additives such as glucose, amino acids or individual corn borer diet components are only slightly phagostimulatory; third, and most important, combinations of ingredients were highly preferred, even when compared with fresh corn tissue. One of these multicomponent additives, the commercial feeding stimulant Coax (CCT Corporation, Litchfield Park, AZ), was the most highly preferred additive tested. When additives were tested under greenhouse conditions (Figure 1), granules containing Coax were more effective at killing corn borer larvae than were granules formulated with corn oil or without additives (6). Under field conditions, the effect of feeding stimulants became more obvious (7). Granules were prepared with Coax at 1 or 10% of solids weight, congo red at 1% (a sunlight protectant (8)) or with no additive. Each of these granules were also formulated with no Btk, 400 IU/mg or 1600 IU/mg of starch dry weight. Field tests were initiated by infesting corn plants with European corn borer larvae and one week later granules were applied over the row with applicators calibrated to deliver 11.2 kg/ha. After 6 weeks, plants were split from base to tassel and the amount of vertical tunneling was recorded (Figure 2). It was concluded that if Coax was present in the formulation, the dose of Btk could be reduced by 3/4 without significant loss of activity. If no Coax was present, the commercially standard dose of 1600 IU/mg was just as effective as the commercial product Dipel 10G (Abbott Laboratories, North Chicago, IL).

Besides reduction of dose, the granular starch formulations also can protect Btk from breakdown due to sunlight (9). Starch granules prepared with potential sunlight protectants retained activity after 12 days exposure to direct sunlight (Figure 3) while those granules without protectants lost their activity within 4 days.

To further test the hypothesis that encapsulation of Btk would prolong residual activity, a series of tests were conducted under field conditions. Granules were prepared with no additive, Congo red, or Coax and placed in the whorls of corn plants. At 1, 2, 4, 6, 8, 10, and 12 days, granules were recovered and assayed with a droplet technique (10). For the assay, granules were digested with amylase to release the bacteria and neonate corn borer larvae were subsequently allowed to imbibe from droplets of the suspension. Larval mortality was assessed 2-3 days later. This experiment was conducted for three years, each with different weather conditions. In all three years, temperatures

were not unusual for the period of the test. However, rainfall did vary. In 1989, no rain occurred and no differences were observed overall, among the granules. That is, the starch granules did not necessarily protect Btk better than a commercial formulation (Dipel 10G) which is prepared by coating corn grit with spores and crystals. However, in 1990, when rain occurred the night after application of granules, Dipel 10G lost a significant amount of activity compared with the starch granules. Over the course of the 12 days, starch treatments were significantly more effective than was the Dipel 10G. In 1991, rain fell 5 days after application. In this year, Dipel 10G was intermediate in activity as certain starch formulations were better than Dipel 10G (Table 1). These data are somewhat contrary to previously published reports describing loss of activity of Btk after application to foliar surfaces. Residual activity of granules in whorls of corn, however, has not been previously measured and different factors may be involved with loss of activity. Measurement of sunlight in the whorl of the plants helps to examine the differences between foliar surfaces and whorls (Figure 4). Clearly, there is very little sunlight penetrating into the whorl of the plant and almost no ultraviolet light. The importance of providing UV protection for granules in the whorl of the plant may be less than previously believed. However, a definite benefit was observed when rain occurred. Starch granules encapsulating Btk were superior in retaining insecticidal activity compared with the commercial granule.

In addition to Btk, other insect pathogens have been successfully encapsulated with the Miragel/water formulation. A *Heliothis* nuclear polyhedrosis virus (11), and a grasshopper entomopoxvirus (12) were both shown to survive this encapsulation process. Field tests with the grasshopper virus formulated with Miragel, molasses, corn oil, and charcoal demonstrated that grasshoppers would feed on the granules and become infected with the virus (13).

Adherent Granules

One of the drawbacks to the Miragel/water formulation process was the amount of water that was necessary to form the granules. Even at a 1:1 ratio of starch and water, the amount of grinding and drying (without heat) that was necessary to finish the granules placed an enormous burden on scaling up the process. Therefore, we initiated a study to determine if the amount of water going into the formulation could be reduced. By simply reducing the amount of water, an unacceptable product consisting of a few large pieces and a lot of dust was created. However, by mixing the water with alcohol, the water became dispersed and consistent mixing was possible. Propanol (15 ml), which will not gel the starch, was mixed with 35 ml water and added to 50 g Miragel. Upon mixing, individual particles formed that required no grinding and little drying. Tests of biological and physical properties demonstrated no loss of activity of Btk (Table 2) and an interesting property of adherence to surfaces (Table 3) (14). Apparently, as granules are formed during mixing, they become coated with a small amount of ungelled starch. Upon contact with moist surfaces, this ungelled starch gels and acts to glue the granule onto the surface. During retrogradation of the starch, the glued particle becomes insoluble and resists wash-off by simulated rainfall.

In addition to propanol, other solvents such as ethanol, butanol, and acetone were effective in dispersing the water. Besides solvents, other water additives could be used. Salts, sugars, plant tissue and insect tissue have all been found to be excellent water dispersers (15). For example, $CaCl_2$ (90 g) was dissolved in 60 ml water. Eight ml of this solution was added to 26 g Miragel and mixed to form discreet granules. Therefore, the total amount of water was reduced from 26 ml to approximately 4.4 ml and still, discreet granules with Btk could be formed. In addition, we have determined that Miragel, which sells for approximately US \$1.55/kg could be replaced with pregelatinized corn flour which sells for about US \$0.55/kg without loss of activity. In fact, feeding preference tests demonstrated that granules made with flour (which contains about 10% protein and 90% starch) were actually preferred over granules made with Miragel (Table 4) (16). Granules formulated in this manner should have all the same attributes as granules formulated with excess water, i.e., incorporation of sunscreens and feeding stimulants, and resistance to washout by rainfall. Field tests to determine efficacy against European corn borer conducted in 1992 with the adherent granules demonstrated that the granules were effective formulations (Figure 5).

Sprayable Formulations of *Bacillus thuringiensis*

While the use of granular formulations of biopesticides is widespread and growing, the vast majority of pesticides are applied as sprayable formulations. Most are composed of dispersing agents to help suspend the particulate Btk in the spray tank. Also, spreader-stickers are added to the tank to enhance application of the formulation. These formulations are particularly

sensitive to degradation by sunlight and washoff by rainfall (17). In 1990, McGuire and Shasha (18) reported on a novel spray formulation consisting of a mixture of Mirasperse (a pregelatinized starch similar to Miragel) and sucrose. When mixed at 2-4% of the weight of water and sprayed onto cotton plants the Mirasperse-sucrose combination effectively resisted washoff by simulated rainfall in the greenhouse. Under the simulated rainfall conditions, Dipel 2X lost activity quickly. However, when the Mirasperse-sucrose formulation was added to the tank mix, more than 80% of the original insecticidal activity was retained after seven days (18). Field tests conducted since the manuscript appeared have supported the greenhouse data. Tests of residual activity on cabbage leaves as well as full season insect control have demonstrated the utility of the formulation.

Tests of efficacy and residual activity of the spray formulations were conducted in cooperation with the Illinois Natural History Survey, Champaign, IL, in 1989, 1990, and 1991. In 1989 (19), three formulations were tested; Mirasperse/Sucrose, Mirasperse/Sucrose + Congo red (at 1% spray solids), and Mirasperse/sucrose + Coax (at 10% spray solids). All formulations contained Mirasperse/sucrose at 4% of the weight of the water; e.g., 25 liters water and 1 kg solids. Cabbage was sprayed at approximately weekly intervals, spray volume was 270 liters/ha and level of Btk was 16 billion IU per acre. At the end of the study, cabbage was evaluated on a scale of 1-6 (20) with 1 representing a perfect head and 6 representing a thoroughly damaged head. Heads rated above 3 are considered as unmarketable in the fresh market. The results of this study (Table 5) suggested that the starch formulations provided season long control of insect pests better than Dipel 2X, a commercial formulation of Btk and as well as Ambush, a pyrethroid insecticide. To examine residual activity, cabbage leaves were brought into the laboratory and fed to diamondback moth larvae (*Plutella xylostella*) at 0, 3 and 5 days after application. In these tests (Table 6), all formulations performed equally well after 1 and 3 days of exposure in the field. However, after 5 days, only the starch formulations retained significant levels of activity. Additives to the formulation did not affect residual activity significantly so, apparently, the starch and sucrose provided protection for the active agent.

Due to responses from industry, the next tests were conducted with lower levels of solids and with flour instead of Mirasperse. In 1990 (21), similar tests were conducted with a pregelatinized flour designated Film Former A by Illinois Cereal Mills. This was mixed with sucrose in a 1:1 ratio and added to the spray tank at 1% solids. Because no effect was observed due to additive in the previous year, nothing else was added to the spray tank. Results from this study revealed that 1% solids did not provide season long control or extend residual activity (Table 7) any better than the commercial formulation, Dipel 2X. Head ratings for the cabbage treated with the flour-sucrose formulation averaged 2.63 whereas ratings for Dipel 2X treated plots averaged 2.33. Control plants averaged a rating of 5.43. Therefore, in 1991, field tests were conducted with solids levels of 1, 2, and 4% with a different flour (designated 22191) with and without charcoal as a sunlight screening agent (22). Unfortunately, this test was confounded by periods of rain which prevented timely applications of pesticides. Therefore, season long control results indicated that cabbage treated with all formulations averaged ratings of more than 5 as heads were damaged beyond market requirements. However, results from two residual activity bioassays revealed that residual activity was related to percent solids in the spray volume. Formulations with 4% solids protected Btk better than formulations with less solids and a commercial formulation (Table 8). Apparently, 4 percent solids is required to form a film thick enough to protect the active ingredients. As an additive, charcoal did not have any dramatic effect on retention of activity.

Summary

In conclusion, starch formulations can be used to extend and enhance the activity of *Bacillus thuringiensis*. Granular formulations are particularly effective when used in periods of rain when retention of active agent within a bait is necessary. Similarly, sprayable formulations are effective at relatively high concentrations and could probably be effectively used for aerial applications or where spray volumes are low. Work is continuing in our laboratory with reducing solids content and extending the technology to formulate insect pathogens from other groups.

References

1. Steinhaus, E.A. 1949. Principles of Insect Pathology, McGraw-Hill, New York.

2. Beegle, C.C. and T. Yamamoto. 1992. Invitation Paper (C.P. Alexander Fund): History of *Bacillus thuringiensis* Berliner research and development, The Canadian Entomologist 124:587-616.

3. Beegle, C.C., H.T. Dulmage, D.A. Wolfenbarger, and E. Martinez. 1981. Persistence of *Bacillus thuringiensis*-var-*kurstaki* insecticidal activity on cotton foliage. Environmental Entomology 10:400-401.

4. Pozsgay, M., F. Fast, H. Kaplan, and P.R. Carey. 1987. The effect of sunlight on the protein crystals from *Bacillus thuringiensis* var. *kurstaki* HD1 and NRD 12: a raman spectroscopic study. Journal Invertebrate Pathology 50:246-253.

5. Dunkle, R.L., and B.S. Shasha. 1988. Starch-encapsulated *Bacillus thuringiensis*: A potential new method for increasing environmental stability of entomopathogens. Environmental Entomology 17:120-126.

6. Bartelt, R.J., M.R. McGuire, and D.A. Black. 1990. Feeding stimulants for the European corn borer (Lepidoptera: Pyralidae): Additives to a starch - based formulation for *Bacillus thuringiensis* Berliner. Environmental Entomology 19:182-189.

7. McGuire, M.R., B.S. Shasha, L.C. Lewis, R.J. Bartelt, and K. Kinney. 1990. Field evaluation of granular starch formulations of *Bacillus thuringiensis* against *Ostrinia nubilalis* (Lepidoptera: Pyralidae). Journal Economic Entomology 83:2207-2210.

8. Shapiro, M. 1989. Congo red as an ultraviolet protectant for the gypsy moth (Lepidoptera: Lymantriidae) nuclear polyhedrosis virus. Journal Economic Entomology 82:548-550.

9. Dunkle, R.L., and B.S. Shasha. 1989. Response of starch - encapsulated *Bacillus thuringiensis* containing ultraviolet (UV) screens to sunlight. Environmental Entomology 18:1035-1041.

10. Hughes, P.R., and H.A. Wood. 1981. A synchronous peroral technique for the bioassay of insect viruses. Journal Invertebrate Pathology 37:154-159.

11. Ignoffo, C., B. Shasha, and M. Shapiro. 1991. Sunlight-UV protection of the *Heliothis* nuclear polyhedrosis virus through starch-encapsulation technology. Journal Invertebrate Pathology 57:134-136.

12. McGuire, M.R., D.A. Streett, and B.S. Shasha. 1991. Evaluation of starch encapsulation for formulation of grasshopper (Orthoptera: Acrididae) entomopoxviruses. Journal Economic Entomology 84:1652-1656.

13. Onsager, J.A., D.A. Streett, and S.A. Woods. 1989. Grasshopper pathogen field evaluation: virus. USDA-APHIS-PPQ Grasshopper Integrated Pest Management Project Annual Report 220-228.

14. McGuire, B.S., and B.S. Shasha. 1992. Adherent starch granules for encapsulation of insect control agents. Journal Economic Entomology 85:1425-1433.

15. Shasha, B.S., and M.R. McGuire. 1992. Adherent starch granules, U.S. Patent Appl. S/N 07/913,565.

16. Gillespie, R.L., M.R. McGuire, and B.S. Shasha. 1994. Palatability of flour granular formulations to European corn borer larvae (*Ostrinia nubilalis* (Hubner); Lepidoptera: Pyralidae). Journal Economic Entomology 87:452-457.

17. Morris, O.N. 1983. Protection of *B. thuringiensis* from inactivation by sunlight. The Canadian Entomologist 115:1215-1217.

18. McGuire, M.R., and B.S. Shasha. 1990. Sprayable self-encapsulating starch formulations for *Bacillus thuringiensis*. Journal Economic Entomology 83:1813-1817.

19. Kinney, K.K., H. Oloumi-Sadeghi, and K.L. Steffey. 1989. Illinois Insecticide Evaluations Forage, Field, and Vegetable Crops 61-67.

20. Greene, G.L., R.B. Genung, R.B. Workman, and E.G. Kelsheimer. 1969. Cabbage looper control in Florida: a cooperative program. Journal Economic Entomology 62:798-800.

21. Oloumi-Sadeghi, H., M.E. Gray, and K.L. Steffey. 1990. Insect Management and Insecticide Evaluations, Illinois 90-96.

22. Oloumi-Sadeghi, H., M.E. Gray, Steffey, K.L., and C.E. Eastman. 1991. Insect Management and Insecticide Evaluations, Illinois 121-131.

Table 1. Original activity remaining of granules formulated with *Bacillus thuringiensis* and exposed for 12 days in the whorls of field-grown corn[a]

Treatment[c]	Average Original Activity Remaining[b]		
	1989	1990	1991
No additive	79.8 a	56.9 b	45.7 bc
Congo Red	63.5 b	45.8 b	62.9 a
Coax 1%	66.7 b	56.7 b	57.5 ab
Coax 10%	90.5 a	77.2 a	52.5 abc
Dipel 10G	87.3 a	22.5 c	40.4 c

[a]Granules were assayed by allowing European corn borer neonate larvae to feed on droplets of the digested granules. Four samples were taken for each granule type 1, 2, 4, 6, 8, 10, and 12 days after plant inoculation.

[b]Means within a column followed by the same letter are not significantly different ($P<0.05$, Least squares means procedure).

[c]Additives were made to Miragel granules during the formulation process. Dipel 10G is a non-encapsulated commercial product used as a control for this study.

Table 2. Effect of encapsulating *Bacillus thuringiensis* in 2-propanol-containing starch granules on percent mortality of *Ostrinia nubilalis*

Trial	Percent mortality	
	With propanol	Without propanol
1	52	48
2	42	48
3	40	43
4	23	52
5	55	43

$\underline{P}=0.53$ (Paired t-test)

Table 3. Effect of organic solvent type on adherence of miragel granules

Solvent[a]	Mean % loss (SD) of granules from slides (n=5)[b]	Mean % loss (SD) of granules from cotton leaves (n=10) Days after application[cd]	
		0	7
Water	100.0 (0.0)a	48.2 (26.7)a	91.9 (9.2)a
2-propanol	2.3 (1.4)f	8.1 (11.9)cd	44.3 (13.7)d
Methanol	82.9 (1.8)b	21.4 (15.1)b	76.3 (16.4)b
Ethanol	13.3 (6.7)de	6.1 (3.6)d	52.9 (17.8)cd
n-butanol	10.4 (2.1)e	4.0 (2.8)d	47.9 (21.2)cd
Acetone	39.3 (1.5)c	13.7 (10.3)bcd	75.9 (21.6)b
1,4-Dioxane	18.3 (7.2)d	19.4 (6.4)bc	60.4 (17.1)c

[a]Granules were prepared by mixing 50 g Miragel with 35 ml water and 15 ml solvent.

[b]Glass microscope slides were wetted with distilled water and then granules were applied. After drying, slides were rewetted by allowing 40 ml water to flow over the slide in a 2 minute period. Slides were air-dried and the washing procedure was repeated three more times. Slides were then weighed to determine granule loss.

[c]Cotton leaves were wetted and granules were then applied. After drying, 0-day leaves were harvested and granules were removed by scraping. Granules were then dried and weighed. A simulated rain treatment was applied to the other leaves by spraying approximately 5 ml water onto the leaf three times over the seven day period. Leaves were then harvested and granules weighed as above.

[d]Means within a column followed by same letter are not significantly different (Least Significant Difference $P<0.05$).

Table 4. Feeding preference of European corn borer larvae allowed a choice between two granule formulations[a]

Granule A	Granule B	Percent of larvae on: A	B
Miragel + $CaCl_2$	Flour 961 + $CaCl_2$	23	77
Miragel + $CaCl_2$ + Coax	Flour 961 + $CaCl_2$ + Coax	29	71
Miragel + $CaCl_2$ + Coax	Flour 961 + $CaCl_2$	25	75
Miragel + $CaCl_2$	Flour 961 + $CaCl_2$ + Coax	15	85

[a]Larvae were placed in petri dishes with a pile of granules at location A and B. After 16 hours, dishes were frozen and the number of insects at each site were recorded. Percentages based on five dishes per comparison.

Table 5. Effect of misasperse/sucrose sprayable formulations of *Bacillus thuringiensis* on protection of cabbage from insect pests

Treatment	Mean Injury Rating[a]	Mean Percentage Marketable Heads[b]
Starch/Sucrose	1.98 ab	82.5 a
Starch/Sucrose + Congo Red	1.48 a	95.0 a
Starch/Sucrose + Coax	1.58 ab	92.5 a
Dipel 2X	2.23 b	82.5 a
Ambush [c]	1.35 a	100.0 a
Untreated	5.03 c	0.0 b

[a]Based on a head rating scale of 1-6 [20]. Means followed by same letter are not significantly different (Fisher's least significant difference test, $P<0.05$).

[b]Heads rated at higher than 3 are not suitable for fresh market. Means as in previous column.

Table 6. Residual activity of *Bacillus thuringiensis* formulations on cabbage leaves, 1989

Treatment	Mean Percentage Mortality[a] Days After Application 0	3	5
Starch/Sucrose	100.0 a	100.0 a	88.0 a
Starch/Sucrose + Congo Red	100.0 a	100.0 a	84.0 a
Starch/Sucrose + Coax	100.0 a	100.0 a	90.0 a
Dipel 2X	100.0 a	87.0 b	22.0 b
Untreated	3.3 b	15.3 c	0.0 c

[a]Diamondback moth larvae were enclosed in dishes containing cabbage foliage selected from treated plants. Means are based on five dishes with five larvae per dish. Means followed by same letter are not significantly different (P<0.05 Fisher's least significant difference test).

Table 7. Residual activity of *Bacillus thuringiensis* formulations on cabbage leaves, 1990

Trial 1

Treatment	Mean Percentage Mortality[a] Days After Application 0	3[b]	5
Flour/sucrose	98.1 a	47.7 a	5.0 a
Dipel 2X	97.0 a	52.3 a	4.1 a
Untreated	2.0 b	0.0 b	0.0 b

Trial 2

Treatment	Mean Percentage Mortality Days After Application 0	3	5	7[c]
Flour/sucrose	100.0 a	90.8 a	32.1 a	12.9 a
Dipel 2X	99.0 a	58.6 b	14.9 ab	2.0 b
Untreated	14.1 b	3.0 c	5.1 b	5.0 ab

[a]Diamondback moth larvae were enclosed in dishes containing cabbage foliage selected from treated plants. Means are based on five dishes with five larvae per dish. Means followed by same letter are not significantly different (P<0.05 Fisher's least significant difference test).

[b]19 mm rain fell on the test plants before the 3 day test.

[c]20 mm rain fell on the test plants before the 7 day test.

Table 8. Residual activity of *Bacillus thuringiensis* formulations on cabbage leaves, 1991

Trial 1

Treatment[b]	Mean Percentage Mortality[a] Days After Application 0	3	5	7
1% Solids	100.0 a	97.5 a	72.5 bc	63.5 bc
2% Solids + Charcoal	100.0 a	90.0 a	88.8 ab	53.0 c
2% Solids	100.0 a	89.7 a	81.0 ab	75.0 ab
2% Solids + Charcoal	100.0 a	90.0 a	90.0 ab	60.0 bc
4% Solids	100.0 a	93.8 a	94.4 a	81.8 ab
4% Solids + Charcoal	100.0 a	97.5 a	93.8 a	89.6 a
Dipel 2X	100.0 a	70.0 b	57.8 c	51.3 c
Untreated	35.3 b	2.5 c	1.3 d	8.5 d

Trial 2

Treatment	Mean Percentage Mortality Days After Application 1	3	6[c]	8[d]
1% Solids	100.0 a	100.0 a	60.5 d	56.3 bc
2% Solids + Charcoal	100.0 a	100.0 a	76.7 bc	43.8 c
2% Solids	100.0 a	95.9 a	82.3 ab	45.3 c
2% Solids + Charcoal	100.0 a	100.0 a	95.0 a	67.5 bc
4% Solids	100.0 a	100.0 a	86.3 ab	71.1 ab
4% Solids + Charcoal	100.0 a	100.0 a	89.6 ab	92.5 a
Dipel 2X	100.0 a	96.3 a	62.1 cd	61.3 bc
Untreated	8.8 b	11.3 b	11.5 d	5.1 d

[a]Diamondback moth larvae were enclosed in dishes containing cabbage foliage selected from treated plants. Means are based on five dishes with five larvae per dish. Means followed by same letter are not significantly different ($P<0.05$ Fisher's least significant difference test).

[b]Percent solids refers to amount of flour and sucrose mixture added to the spray tank. Charcoal, if present, was added at 1% of the solids content.

[c]51 mm rain fell before the 6 day test.

[d]2 mm rain fell before the 8 day test.

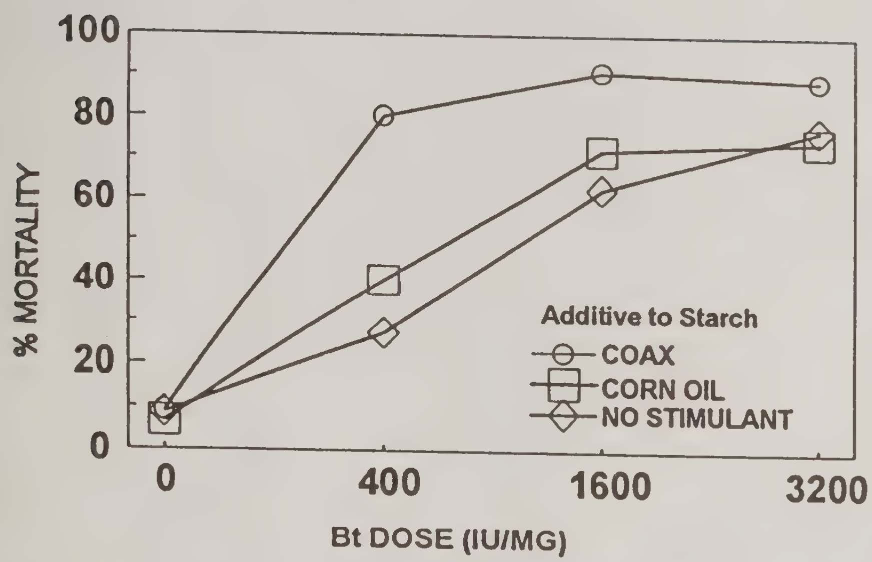

Figure 1. Response of European corn borer larvae to starch formulations of formulations of *Bacillus thuringiensis* treated with different feeding stimulants. Greenhouse-grown corn plants were treated with 75 mg granules and then egg masses were pinned to the whorl. Plants were dissected 5 days later and percentage mortality was obtained. Numbers represent means of 5 plants per formulation (6).

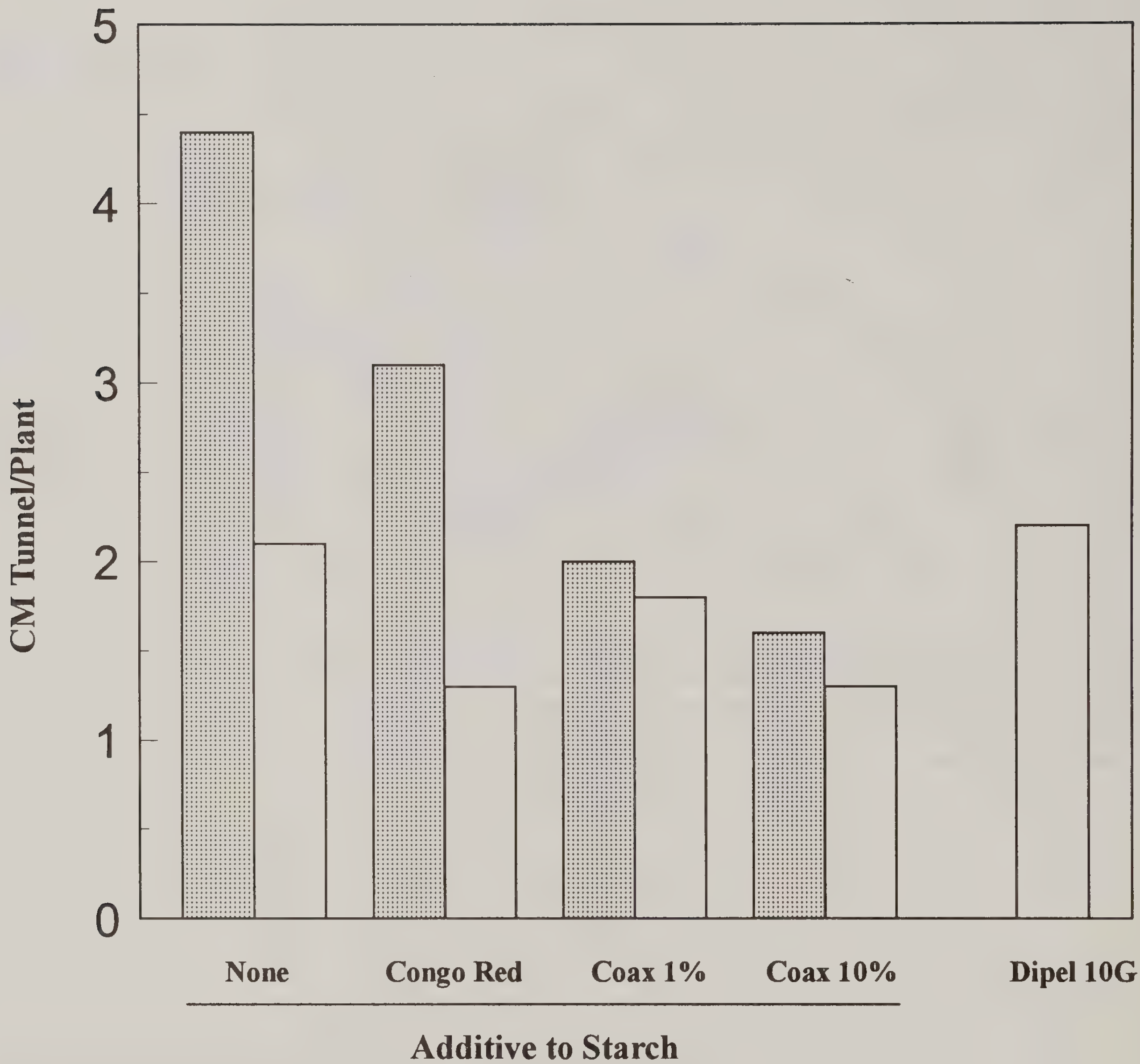

Figure 2. Efficacy of starch formulations of *Bacillus thuringiensis* applied to field corn. Corn was infested with European corn borer neonate larvae and then treated with granules. Six weeks later, stalks were split and length of tunnels measured. Untreated controls are not shown but averaged 12 cm per plant. Shaded bars represent granules formulated at 400 IU Btk/mg dry weight, unshaded bars represent formulations made with 1600 IU/mg. Note that in the presence of Coax, rate of Btk can be reduced without significant loss of efficacy (7).

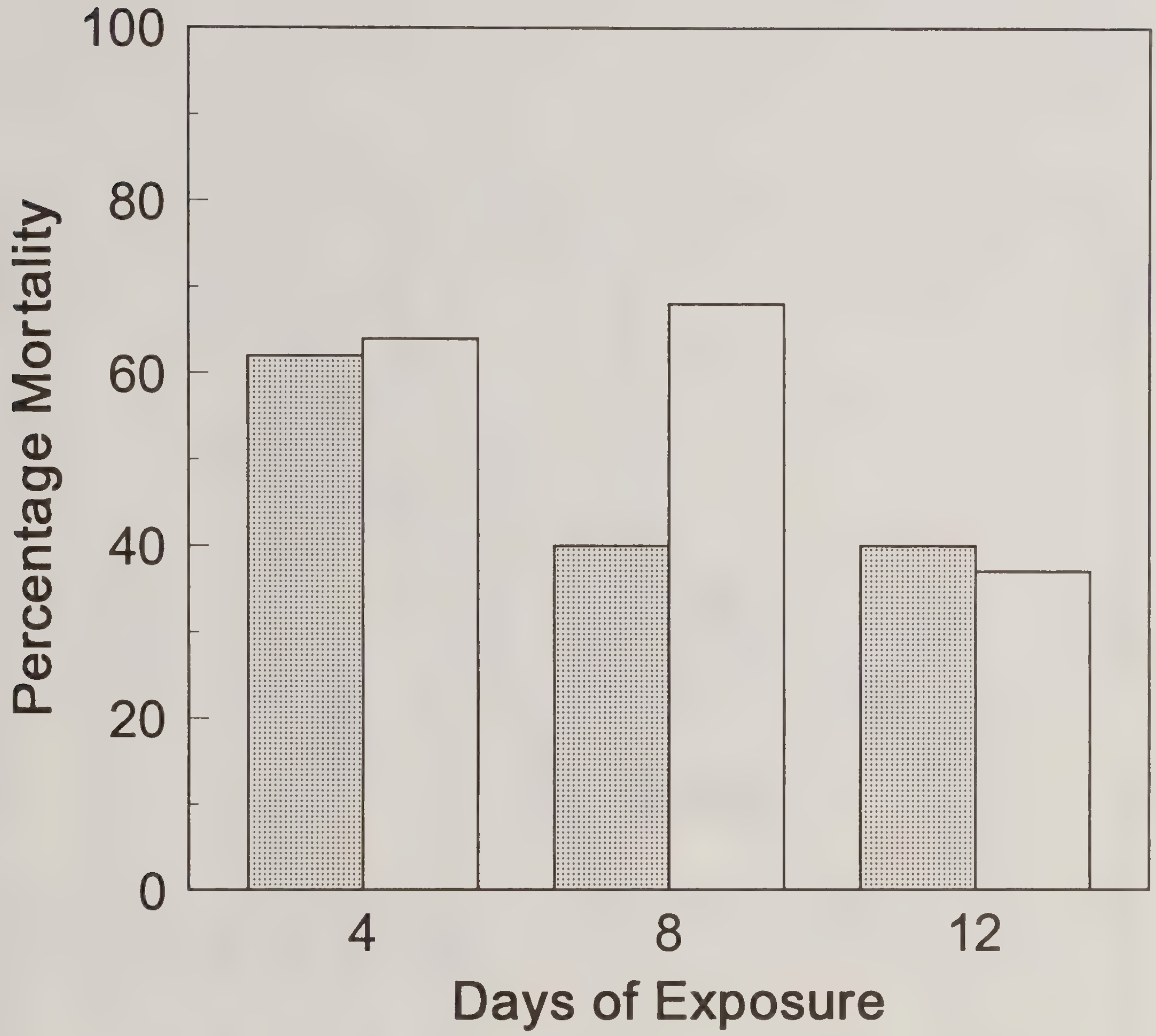

Figure 3. Protection of *Bacillus thuringiensis* from sunlight. Starch formulations were made with either 0.1% (shaded bars) or 1% (unshaded bars) of sunlight protectants and exposed to direct sunlight. Granules were then assayed for biological activity against European corn borer neonate larvae. Granules without protectant lost all activity before the four day sample and are not shown (after 9).

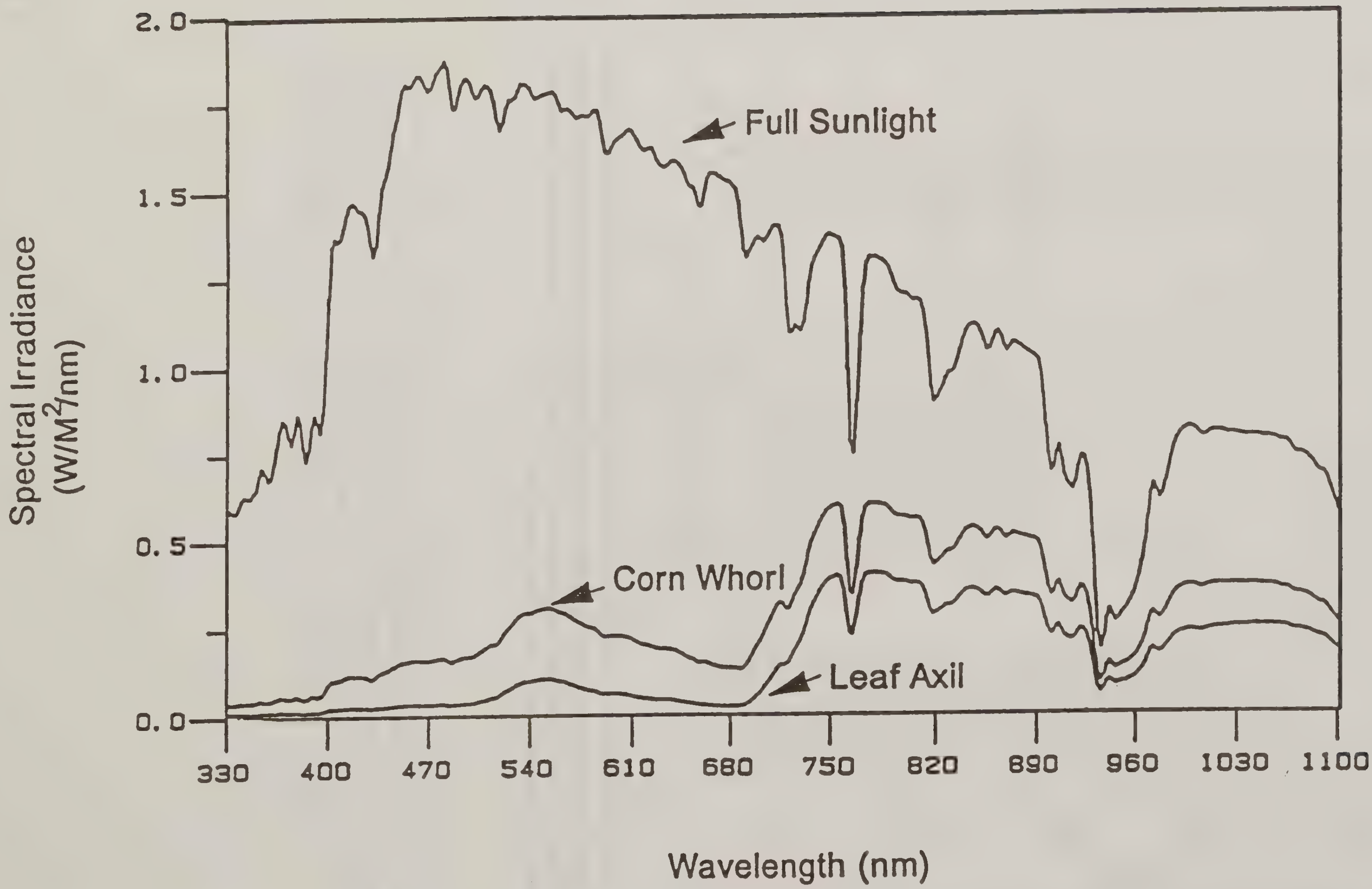

Figure 4. Sunlight penetration of corn foliage. Very little light, especially in the UV range penetrates into the whorl or behind the leaf axils of corn plants. Readings taken with a Li-Cor portable spectroradiometer fitted with a remote cosine receptor.

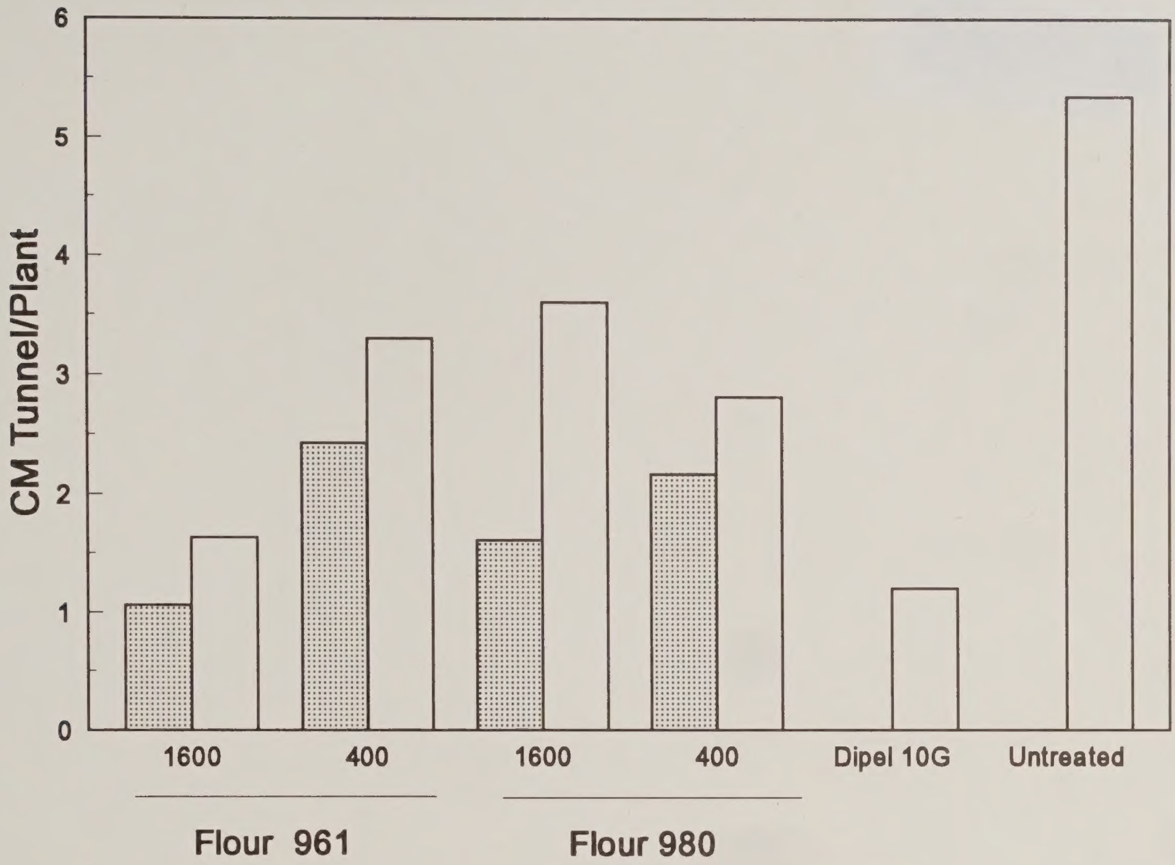

Figure 5. Efficacy of adherent starch granule formulations for control of European corn borer larvae in the field. Granules were formulated with Flour 961 or flour 980, with 1600 or 400 IU/mg and with Coax (shaded bars) or without Coax (unshaded bars).